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Science & Technology

USSR: Chemistry

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FBIS 50th Anniversary Note

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We members of the current staff of FBIS extend our thanks to consumers for their interest in FBIS products. To past staffers we extend our thanks for helping the service reach this anniversary year. At the same time, we pledge our continued commitment to providing a useful information service.

R. W. Manners
Director
Foreign Broadcast Information Service

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SCIENCE & TECHNOLOGY

USSR: CHEMISTRY

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Present and Future Metal Complex Synthesis

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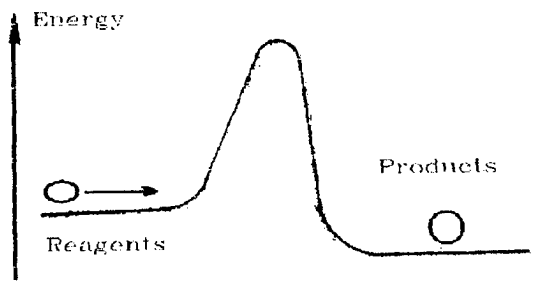
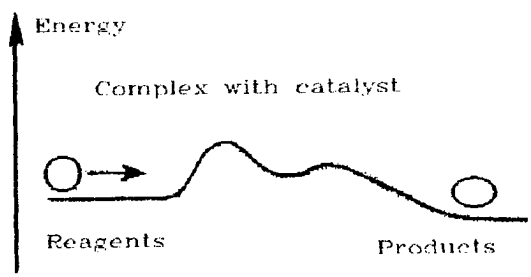
[Article by G. B. Shulpin, candidate of chemical sciences]

[Text] Chemists have been studying the phenomenon of catalysis for about 150 years now, and in that time many thousands of catalysts--accelerators of chemical reactions--have been synthesized, studied and introduced into industry. The great majority of catalysts known today are solids: metals, alloys, and minerals. The initial materials, in solution or in the form of gases, react on the surface of these catalysts. This is what is called heterogeneous catalysis. On the other



Model of noncatalytic reaction that takes place with liberation of energy



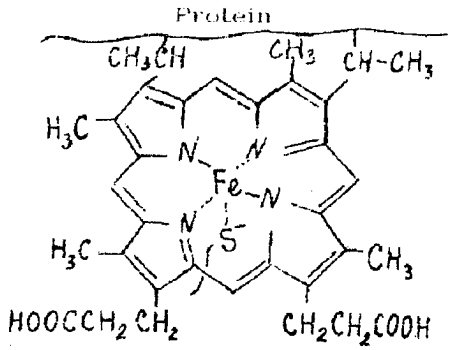
Model of catalytic process

hand, if both the reacting substances and the catalyst are in solution, it is called homogeneous catalysis. In this case, the catalysts are most often metal complexes. I am going to try to talk about what they can do in chemistry (and not only in chemistry).

Homogeneous or metal complex catalysis is a relatively young field of chemistry. In essence, its age does not exceed three decades. But the object of its research has existed on the earth for a least four billion years. The fact is that chemists are just beginning to learn model reactions that occur extremely readily in living cells under the action of biological catalysts--enzymes. It is no wonder that specialists in the field of metal complex catalysis are turning to nature as a teacher. After all, many enzymes contain metal ions that in fact catalyze the molecules in cells.

Catalysts in the Living Cell

One of these is the oxygen molecule. The O_2 is activated in the organism by enzymes that contain heme. This is a complicated structure with an iron ion is in the center of the molecule. When attached to proteins, heme forms what is called cytochrome P-450--an enzyme that par-



Conventional depiction of enzyme molecule containing heme

ticipates in oxidation of organic substances in the cell. Cytochrome P-450 attaches a molecule of oxygen to the cell. It is as if the bond between oxygen atoms is loosened, and the molecule is activated. Then with the help of a biological reducing agent, one oxygen atom forms a water particle, while the other is incorporated into a hydrocarbon molecule. The resultant alcohol is readily liberated from the organism. For example, cytochrome assists in neutralizing harmful saturated hydrocarbons in the liver of higher animals.

Heme bound to another protein is capable of performing a different role. In this case, it does not react with an oxygen molecule, but merely attaches itself temporarily to an iron ion. Oxygen travels through the cell in this form, readily splitting off wherever needed. The reader has no doubt guessed that I am talking about hemoglobin.

Chemists have recently proposed a set of fairly simple metal complex catalytic systems that allow enzyme operation to be modeled. Here is an example: a system developed at the Institute of Chemical Physics, USSR Academy of Sciences, enables conversion of nitrogen to ammonia under mild conditions, i.e. it gives a good imitation of the operation of the natural enzyme nitrogenase.

And the action of cytochrome P-450 can be modeled by a simple chemical system if a porphyrin iron complex is used as the catalyst and ascorbic acid is used as the reducing agent.

Great Significance of Small Molecules

A preeminent role is played in our life by substances made up of simple molecules of small (comparatively, of course) size. These are oxygen, nitrogen, carbon dioxide and methane. At the same time, even a beginning chemist knows that these substances react rather reluctantly under ordinary conditions. Homogeneous catalysis can activate small molecules, yielding valuable products. Recently, late last year in Leningrad a symposium was held on metal complex catalysis. It was especially devoted to activation of small molecules.

It must be said that of all the aforementioned substances, only oxygen is effectively used in wide-scale industrial processes that are catalyzed by complexes. For example, oxidation of ethylene yields its oxide, which is used in production of a number of materials such as acrylonitrile. Interaction of cyclohexane with oxygen when catalyzed by a cobalt compound ultimately yields adipic acid, from which it is but one step to the polymer nylon. Finally, oxidation of para-xylene yields terephthalic acid--an intermediate in the production of mylar. And this process necessitates participation of a catalyst.

The other aforementioned small molecules have thus far not found application in the chemical industry. The fact is that the first reactions of activation of nitrogen, carbon dioxide and methane by complexes have just recently been discovered.

Academician Mark Yefimovich Volpin feels that one of the most amazing advances in homogeneous catalysis is the discovery of the capability of metal complexes to activate inert molecules. Just a quarter of a century ago, chemists were certain that there was no way that nitrogen could be brought into any kind of reaction at a temperature lower than 500°C. Yet today we know that some complexes are capable of binding nitrogen molecules into more or less stable compounds even at -100°C. Nitrogen conversion products are yielded when such compounds are reacted in turn with other substances such as water or acids. And these are very valuable products: ammonia (fertilizer), hydrazine (fuel), and organic amines (intermediates for dye synthesis).

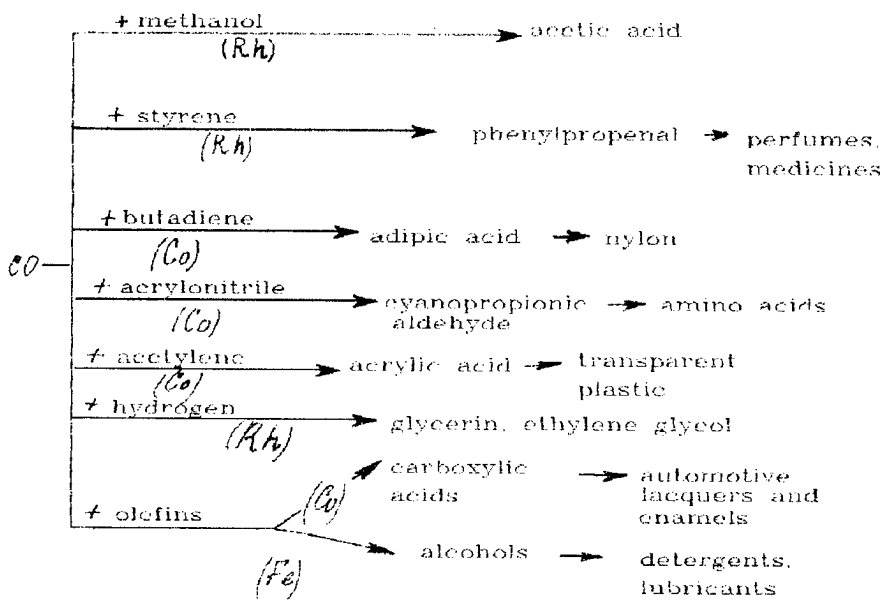
Another example is saturated hydrocarbons, which are something like "chemical corpses." But even here, complexes are capable of destroying

the inertness of the molecules. Activation of the carbon-hydrogen bond enables extensive utilization of methane and other saturated hydrocarbons in industry. For example, synthesis of methyl alcohol from methane in a single stage directly from the gas, of which there are enormous reserves. And methanol means plastics, solvents, and much more.

By "stripping off" long chains of carbon atoms in paraffin or distillation residues, we can synthesize light hydrocarbons, or putting it more simply, gasoline. The first catalytic systems for doing this under comparatively mild conditions were found a few years ago. Complexes of metals like rhenium are the basis of such systems.

It should be said that the world is now paying exceptional attention to research in the field of activation of molecules. Special national programs for such research are being developed in some countries. All this is not merely because of purely scientific interest in the enormous capabilities of complexes in the activation of inert molecules. There is no doubt that small molecules in future will constitute a significant part, if not the main part of the raw material base for both the chemical and the fuel industry. Industrial chemistry will be based on conversions of atmospheric nitrogen, carbon dioxide (a product of fuel combustion), and carbon monoxide produced by processing coal. And even today, valuable products are being produced from carbon monoxide by homogeneous catalysis.

This is what I learned from Academician M. Ye. Volpin, author of the first research on nitrogen fixation, now among the classics.

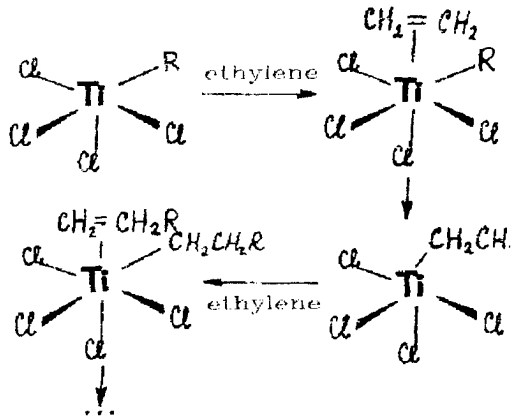


Scheme of catalytic use of carbon monoxide

MOLECULAR SURGERY

Drawing a comparison with the currently popular hero of Moliere who did not know that he was speaking prose, it can be said that we all unknowingly use the fruits of homogeneous catalysis. Catalysis plays a particular role in material production.

In the 1950's, the West German chemist K. Ziegler accidentally discovered that ethylene is very easily converted to a polymer under the action of alkyl derivatives of aluminum and titanium salts. This discovery ushered in the age of polyethylene, which has penetrated into all fields of human endeavor. The reaction of ethylene polymerization is a typical catalytic process.



Catalytic polymerization of ethylene. In the first stage, an organoaluminum compound AlR_3 (R is some alkyl radical) reacts with titanium chloride. An organotitanium compound is formed that is capable of attaching an ethylene molecule. The R group then jumps over to the ethylene molecule, and the ethylene is now joined to the titanium only through a carbon atom. A new free place arises at the titanium atom, a new ethylene molecule is attached to the titanium, and the process is repeated...

Catalysts not only take part in the polymerization process, they are necessary for synthesis of the initial monomer product. One such process, the synthesis of vinyl acetate from ethylene, has been developed by I. I. Moiseyev et al. This reaction can be depicted by a very simple equation:

$$CH_2{=}CH_2 + CH_3COOH \rightarrow CH_2{=}CHOCOCH_3.$$

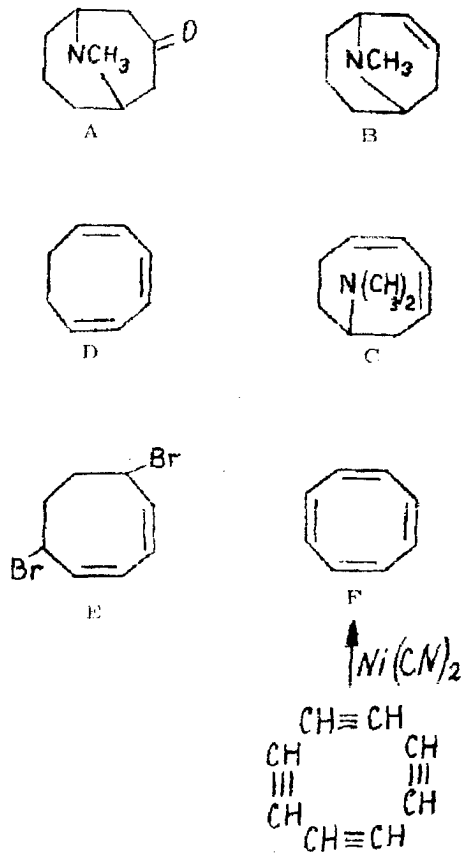
Very valuable products like shatterproof glass and transparent plastics are synthesized from vinyl acetate polymer.

Chemists who deal with the synthesis of organic molecules are a little like surgeons: they have to cut out the bonds between atoms, remove certain groupings from the molecules, transplant new ones in their place, and stitch together molecules or parts of molecules. Naturally, all of these operations would be impossible without the appropriate instruments. "Scalpels," "clamps" and "needles" here are sets of various reactions: oxidation or reduction, formation of rings, substitution or detachment. Medical doctors have recently supplemented their toolbox with innovations that are fundamentally different from anything they have had before. Examples are laser scalpels, and synthetic thread for suturing that is gradually absorbed in the tissues. Continuing our comparison with surgery, let us say that catalysis by complexes considerably extends the arsenal of facilities that allow us to "operate" on molecules.

In our country, interesting work is being done in this field under the guidance of Associate Member of the USSR Academy of Sciences I. P. Beletskaya. For example, it has been possible by using a palladium catalyst to remove alkyl and phenyl radicals and derivatives of tin, mercury and other metals. These groups are transplanted in the place of iodine or chlorine into the molecules of any other organic compounds. Thus organic chemists have received the gift of a new and quite convenient method of synthesizing the most complicated substances, including natural compounds that heretofore could be synthesized only by living organisms. Now we can easily and rapidly produce molecules in which a benzene ring is linked to an acetyl fragment, a ketone group, or to another benzene ring that carries any substituents.

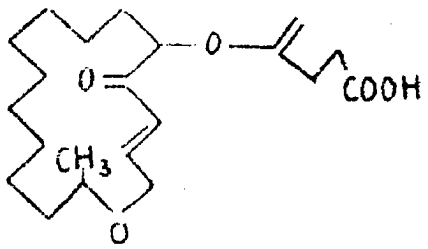
Today we need no longer be concerned about the fate of homogeneous catalysis in other divisions of chemical science. At least, that is the opinion of Irina Petrovna Beletskaya. But in the beginning when homogeneous catalysis was only starting, she recalls, many chemists were not in much of a hurry to make a "skill change" and try themselves out in the new field. And although the first rather simple, and one might say elegant methods of synthesizing organic substances by using metal complexes had been discovered back in the thirties, inorganic chemists went right on occupying themselves with "pure" inorganic chemistry while specialists in the field of organic chemistry preferred to carry out their reactions by using more primary traditional reagents. In kinetic terminology, we might say that an induction period was observed in the development of homogeneous catalysis. And it was not until the sixties that this barely noticeable existence was replaced by a veritable explosion of growth. The fact is that at this time we were getting the first inkling that petroleum reserves were running out, and accordingly many products of petroleum processing were getting scarce. Moreover, this was a time of unusual flowering of organoelemental chemistry. But one way or another, when organic chemists finally gave their attention to homogeneous catalysis, it was found that complexes easily enable single-stage synthesis of substances that were obtained only with great effort in another way. For example, the Japanese chemist Y. Fujiwara has discovered an elegant reaction by which styrene can be synthesized

directly from benzene and ethylene in the presence of a palladium salt. No less impressive is the single-stage synthesis of the hydrocarbon cyclooctatetraene: to prepare it, one need only subject acetylene to the action of a nickel complex. And this compound was once produced from the bark of the pomegranate tree, and then only after complicated chemical conversions consisting of ten stages!



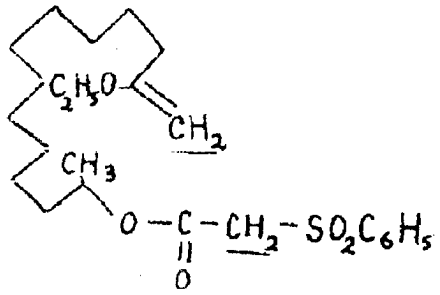
At one time cyclooctatetraene (compound F) was obtained by the exhausting process of multistage synthesis from the alkyloid pseudopelletierine (structure A) extracted in turn from the bark of the pomegranate tree. To do this, A was first reduced, water was split off from the product (stages 1 and 2), the resultant substance B was treated with methyl iodide, then silver hydroxide, and the resultant compound was decomposed by heating (stages 3, 4 and 5). Product C was again introduced into analogous reactions (stages 6 and 7), then bromine was attached to D (stage 8), E was treated with dimethylamine and silver hydroxide and reheated, yielding the required substance F. However, this compound is readily obtained in a single stage by using a nickel catalyst to link four molecules of acetylene

To give an idea of how catalysis by complexes is finding application in synthesis, we give the following example. The mold Penicillium turbatum is known to produce a certain antibiotic that suppresses growth of bacteria and fungi. In contrast to many other antibiotics, such as penicillin, it does not have a name, and is known only by a number: A26771V. Chemists have established the structure of this medication. It has been learned that its molecule is constructed in the form of a 16-member ring (the zigzag on the formula is formed by CH_2 groups):

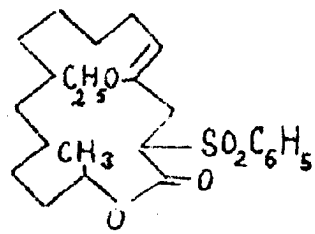


Antibiotic "A26771V"

Can such a complex product be synthesized from simpler products? It can. This is how it was done several years ago by U.S. scientists. The aldehyde 10-undecenal $CH_2{=}CH(CH_2)_8CHO$ was used as the intermediate for the molecule. By using various manipulations in five stages, a product was obtained from it whose name we will not give (it is long and complicated to match the molecule itself). However, we will sketch the formula:



A solution of the substance whose formula is sketched above was boiled for 20 hours with a very small amount of a phosphine complex of zero-valency palladium. The result was that the carbon atoms of two CH_2 groups (they are marked on the formula) were joined, forming a ring:



Now we can easily guess the structure of the antibiotic molecule. In fact, as a result of transformations consisting of several stages, a transition was made from this compound to the medication.

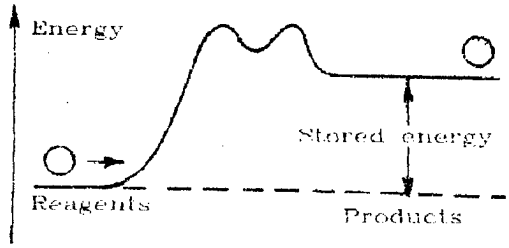
I. P. Beletskaya suggests that we cannot rule out the advent of fundamentally new methods of homogeneous catalysis in the near future. A few years ago, for example, interphase catalysis was realized where two reacting substances are in different immiscible liquids. Almost immediately, this principle was used for catalysis by complexes as well. Right now, it is difficult to say what types of complexes will gain the greatest popularity in catalysis in the future. But it is clear that catalysis will take on greater and greater significance in the synthesis of hormones, vitamins, prostaglandins and other exceptionally important biologicals. And unfortunately, it must be noted here that our nation is still a long way from doing this research on the scale that it should.

How Do You Store Solar Energy?

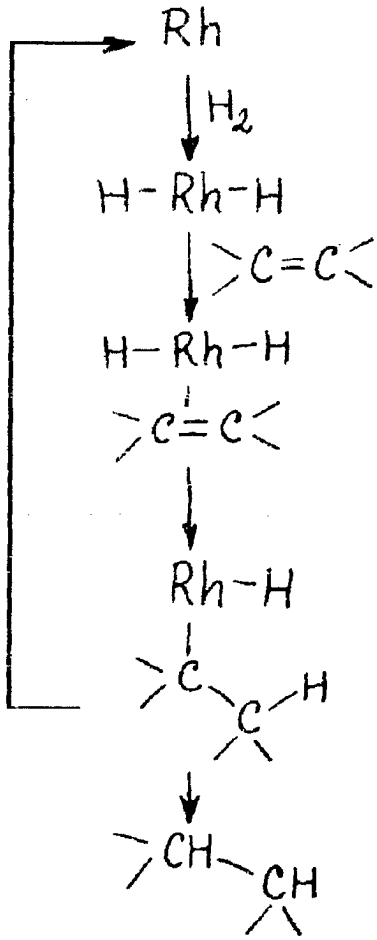
It is an eternal question. One way to solve it at last is to learn how to carry out photochemical reactions that yield products richer in energy than the initial substances. And perhaps the simplest substance suitable for "canning" the energy of solar light is water. By decomposing it into hydrogen and oxygen, we get just what we needed: energy-rich products. By burning hydrogen in oxygen, we convert this energy into heat. But the problem is that we have not yet learned to split water with minimum energy inputs. However, early results are promising.

For example, catalysts that enable hydrogen to be liberated from water have long been known. And we have recently succeeded in liberating oxygen from water by complexes of ruthenium, iron and cobalt. Such research is being done in our nation by the A. Ye. Shilov and K. I. Zamarayev groups. Let me note that all systems being artificially created ultimately simulate the natural photosynthesis by which plants accumulate solar energy.

Green plants store solar energy and provide food for all life on earth. How intriguing to be able to use reactors in a factory, for example, to synthesize amino acids and use them to make food products or, in order to eat customary food, simply add them to cattle fodder.



Model of catalytic reaction to store energy in chemical compounds



A rhodium complex catalyzes the process of attachment of hydrogen to a double bond. If the catalyst is used in the form of one of the mirror antipodes, the product of attachment will be obtained in the form of only one optical isomer

Synthesis of amino acids presents no great difficulties today. The problem is that protein is made up of amino acid molecules of only one mirror image, and conventional organic synthesis yields an equal mixture of both mirror antipodes. Half of the food prepared from such synthetic amino acids will not be assimilated by the organism.

Metal complex catalysis solves this problem as well. It has been found that in the presence of certain catalysts (e.g., a rhodium complex), hydrogen is attached to the double bond of an unsaturated organic compound on only one side, rather than haphazardly. As a result, only the one necessary stereoisomer of the amino acid is obtained.

This field of homogeneous catalysis is still in the basic research stage. Therefore, publications may be encountered in the science literature with titles that do not say much to the nonspecialist. For example "Complexes of Zero-Valency Palladium With S-(-)-α-phenylethylamine as Catalysts of Enantioselective Reducing Aminolysis of Δ-Oxazolinones-5." Who would guess that the subject is our food of tomorrow? And the whole point is that palladium complexes suggested by the Soviet scientist Ye. I. Klabunovskiy catalyze conversion of these very oxazolinones in such a way that amino acids are synthesized in only one optical form.

"Living" and "Dead" Water

Homogeneous catalysis has found application in conservation of the environment as well. A chemical-biological model of an aqueous medium was created several years ago. In accordance with this model, which was developed by Soviet scientists Yu. I. Skurpatov, A. P. Purmal, and L. S. Ernestova in cooperation with U.S. colleagues, hydrogen peroxide plays an exceptionally important role for normal life activity in a body of water. This substance is formed when oxygen is reduced under the action of solar light or catalysts: metal ions that are always plentiful in natural water.

In addition to peroxide, products of the vital activity of organisms are constantly being released into water. As such substances reduce the peroxide they lower its content in the water. A redox equilibrium is reached. Until recently, a certain surplus of peroxide had been maintained in natural waters, and when certain organic pollutants entered a body of water, a complex mechanism of self-decontamination of water was switched on: the peroxide oxidized the pollutants with the participation of catalysts. Alas, in recent decades the flow of pollutants (e.g. due to washout of chemicals from fields) has increased so much that natural self-decontamination can no longer do its job. Hydrogen peroxide has disappeared, and water has changed from oxidative to reductive. And many aqueous organisms on different stages of development can exist only in an oxidative environment. Thus the water of rivers and lakes has been converted from "living" to "dead."

Conclusions suggest themselves: the reproduction of many valuable species of fish necessitates an increase in the peroxide concentration in natural bodies of water. Such experiments were done several years ago on the Lower Volga at the Volgograd Sturgeon Plant, and gave excellent results. By this means several million sevruga fry were saved and grown. Is this a little or a lot? Before the use of the new method, the survival rate of sevruga larvae at the plant ranged from zero to five percent. Peroxide has raised this index to 90 and even 100 percent.

Back to the Enzyme

Today two-thirds of chemical and oil refinery processes take place with the participation of catalysts, and nine out of ten new technologies use catalysts. Therefore, it is no wonder that a state target scientific and engineering program has been devoted to the problem of developing new catalysts and catalytic processes. It is part of the program package on especially important areas of science and engineering developed by the USSR State Committee for Science and Technology, the State Planning Commission, and the USSR Academy of Sciences. The "Catalyst" interbranch scientific-technical complex has been set up (the director general of the complex is K. I. Zamarayev). This has to do with the organizational aspect of the job.

But it looks as if chemists are going to have to change research procedure as well. Associate Member of the USSR Academy of Sciences A. Ye. Shilov feels that the old division of catalysis into three sections--heterogeneous, homogeneous and enzymatic--is becoming increasingly out of line with the present state of affairs. The creation of so-called organized molecular ensembles constructed after the image and likeness of the enzyme is becoming a reality. And what is important is not what form the catalyst is in (in solution or in solid form), but the method of organization of the molecules in the catalyst complex. "In my opinion," says Aleksandr Yevgenyevich, "it is hard to imagine a field of science that will be as important for man as catalysis. Like enzymes, synthetic catalysts will be able to provide us with materials, energy and food. It can be said that this field of catalysis is a science hurtling into the future." It would be hard to disagree.

Reading List for Metal Complex Catalysis

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Onward -- to the Cave?

907M0319B Moscow KHIMIYA I ZHIZN in Russian No 8, Aug 90 pp 2-5

[A discussion with Mariya Cherkasova, candidate of biological sciences]

[Text] A session of the Joint U.S.-Soviet Commission on Cooperation in the Field of Environmental Protection was held in January of this year in Washington. For the first time, the Soviet delegation included an informal, Mariya Cherkasova, representative of the "Green Party." She is a candidate of biological sciences, has worked for many years at the Institute of Protection of Nature, has worked on the Red Book, and the problem of protection of rare animals. She recently has left science, devoting herself entirely to public ecological activity. She was elected secretary of the Social-Ecological Union, where she feels that efficiency is incomparably higher than it had been at the institute. Our correspondent's talk with Mariya Cherkasova, which began as proposed with questions and answers, was very quickly transformed into her monologue.

What was it that was most striking to me in the United States? Probably the enormous and favorably disposed interest in our country, a sincere desire to understand us, although at times it is simply inconceivable for the the average American to do so. For example, we announced for the record that air pollution is 10 or more times the limiting permissible concentrations in 103 cities of the USSR with a total population of 50 million. When they learned of this, the Americans were shocked and asked why we did not immediately close the offending production facilities. Well, there was no way to explain to them that if we were to start closing such facilities in accordance with norms, then we would have to make short work of nearly all of them, with the odd exception. And the people themselves would rebel against such severe measures: they've got used to it, and where would they work?

Someone asked me with sympathy: "How have you come to a life like that?" And now, looking at what is happening as if from the outside through their eyes, it makes me shudder, and I can't shrug it off. Just think, in fact, about the kind of limbo we live in if limiting permissible concentrations of substances incompatible with life are habitually exceeded by factors of tens, hundreds and thousands!

If the public in the person of some ecological group should dare to demand the closure of a production facility, it is hit with a storm of demagogy, incrimination of "green" extremism, even going as far as being called a "green plague," and some high-placed official is sure to announce with righteous wrath: "Do you want to drive us back into caves?"

And incidentally, it is my opinion that one should not have anything at all bad to say about caves, which once served the human population well, prolonging people's lives, which certainly cannot be said about our modern cities, which do the opposite, sucking the life out of a man.

A film about Sumgait was shown at an All-Union Conference of the Social-Ecological Union held in December of last year. From the screen, a resident calls her city a gas chamber under the open sky. Hundreds of industrial monsters that are superconcentrated on this long-suffering land spew forth tons of liquid, solid and gaseous poisons. Most of the citizens huddle together in dilapidated temporary buildings directly up against these monsters. The [Caspian] Sea has been dead for a long time, you can't swim or fish in it, and Sumgait kids go out to play on the foul-smelling dump. Even if one of them has had the rare luck to be born healthy, just imagine what his spirit has to grow on here! I am convinced that the explosion that started the bloody events in Trans-Caucasia has ecological roots. Not necessarily the slaughter of Armenians, but something dreadful had to happen in this city, it is so brutal.

Now tell me, by comparison with this wouldn't paradise be more like the caves of prehistoric man, who lovingly painted his walls with pictures of the hunt for wild animals? And by the way, they have all disappeared in the environs of Sumgait, with the exception of the most persistent garbage eaters like rats. How people can survive here seems like a miracle. And are they surviving? The same film shows heart-rending scenes taken in the home for Sumagait children with birth defects. One of those present in the room was unable to stand it, and fled to the hall. And whither are the people of Sumgait to go? Who awaits them, and where? There is no end of refugees in our country without ecological refugees. And is it any better in Chelyabinsk, Novokuznetsk, Kirishi, Krivoy Rog, Baykalsk or Bendery?

In the end, we are only kidding ourselves when we say that our country is on the threshold of an ecological crisis. The threshold was long ago crossed, and the crisis is developing at full tilt. In some places it has reached an apogee, or is approaching it. Places are multiplying on the map where living is not only harmful to the health, but is impossible altogether. And not only the radioactive zones resulting from the Chernobyl disaster: the region of Aral has been made incompatible with life; practically the same can be said about the Kuzbass or the Lower Volga.

Indeed, the entire Volga is one long sore. She has symbolized Russia from time immemorial. Even now, violated by gigantic dams, filthy and half-dead, she carries this symbolism. And a multikilometer exclusion zone has had to be placed around the Astrakhan Gas Condensate Plant like around a raging reactor. "We feel constant fear" has been written in a questionnaire by the inhabitants of this region, living in expectation of a gas attack. Gas masks are kept on hand in the houses here, and it

was recently learned that children were put to bed with gas masks on during a routine discharge.

Things are not good at all for the children. At the same December conference of our Union, another film was shown that had been taken in Karelia, in Kostomuksh, not so long ago a mecca for tourists, now dominated by paper-and-pulp combines. All children have been stricken with fluorosis, a condition in which babies develop broken and blackened teeth, and schoolchildren must wear dentures. Not only the teeth are affected, but the skeletal system as well. Children suffer from fluorosis in the Kuzbass as well, and near Astrakhan, this horrible disease is spreading throughout the nation, as is alopecia--childhood baldness. More and more children are coming down with leukemia and cancer. How many little martyrs we have who do not know how to laugh and are constantly coughing from allergies? How many children with diseased kidneys, livers, gastritis, high blood pressure? Doctors have never seen the like before!

Eighty percent of illness is due to bad water, this was heard at a session of the Supreme Soviet of the USSR. The worn-out earth, poisoned with pesticides and fertilizers, cannot bring forth a product fit for consumption when irrigated with such water. The potatoes that I buy at the store in the capital show the state of our earth as in a mirror. I remember with fond sadness the good old potatoes of my wartime childhood, cracking open they were cooked, blossoming out like a rose, fragrant, glistening with beads of starch. You could eat them without anything at all, even without salt, they were so tasty. And we, the wartime children, survived on the potato!

But, my god, what I have to offer my own child, who has never known the tribulations of war! I clean these potatoes with sadness, they are yellow, they smell bad, they are slimy, I immediately throw half of them out with the peelings, and they still turn black when cooked, and I clean them again when they're already done. "I wonder what they're made made of," grumbles my typical allergic Muscovite. "Whatever the poor things could grow on," I reply.

And now, lest I be accused of excess emotionalism, let me appeal to an authoritative opinion. A recent article by D. K. Sokolov, doctor of medical sciences and director of the Department of Studying and Forecasting the Population at the Scientific Research Institute of General and Communal Hygiene, USSR Academy of Medical Sciences, is impressively entitled "On the Road to Degeneracy." This article was published by ENERGIYA late last year. Here is what struck me in particular: If we take the 1938 requirements for army draftees as health guidelines, eight or nine out of 10 soldiers in service today should be immediately discharged! Such is the devastating evolution of only 50 years. More of our people are getting sicker with increasing frequency. There are more and more stillbirths, and among the children that survive birth, more and more are mentally and physically defective. The level of mortality is declining in civilized nations, and ours is rising.

The author sees the main reason for such a devastating situation in the quality of air, water, soil, and food products. He names some other reasons as well. Deterioration of the gene pool, as the entire post-revolutionary history of our nation is a history of annihilation of the best, strongest and most courageous people. Chronic hunger that has lasted for 70 years now: often people die not from diseases but from hidden starvation, a lack of the rich substances needed by the organism.

"Terrible?" Dmitriy Konstantinovich echoed when I phoned him after reading his article. "That's just what got past the editors! But the worst of it is that we are accumulating a genetic 'burden.' We have now nearly reached a fatal line, just a little further and there will be no turning back, an uncontrollable process will begin, genetic disaster!"

Indeed, it is much worse. And if we dig around for reasons, they are ecumenical in part: the scientific-technical revolution has been accomplished at severe ecological cost for the entire world. But our version is the most severe. We are now reaping the bitter fruits of development of our socialist state and its devil-may-care attitude toward man. The yardstick of progress has become billions of kilowatt-hours of electrical energy, millions of tons of petroleum, coal, steel, millions of cubic meters of timber, thousands of kilometers of pipelines, and all of it at any cost! After wasting colossal natural and human resources, not only have we got no richer, we are many times poorer. And if we have been accustomed to say that "they" have a user society, then ours with complete justification can be called a destroyer society.

Saddest of all is that so far everything is staying just as it was. We are sticking to the former plan oriented toward extensive quantitative growth of production, chiefly industrial. Hence we get gigantomania, a set toward "excavation pit" supersites that gobble up scads of money and natural resources. Hence we get continued ravaging of the country and continual growth of waste, total pollution of the environment. For practical purposes, agencies are waging war against their own people.

I would say that open Stalinist genocide is being replaced in our day by a more subtle and veiled modification: via ecocide, destruction of the environment needed for life. Being a specialist in zoology, I know full well that there is no surer way to destroy a species than by depriving it of its place to live.

How many plans conceived in bygone days have been zealously pushed through! The country has no money, not even for getting children out of zones stricken by irradiation. But for plans like this--go right ahead!

Take the Katunki Hydroelectric Plant: three expert evaluations one after the other showed it to be economically ridiculous, ecologically and socially hazardous. A protest movement sprang up throughout the nation, and the plan was put through another expert evaluation, hanging on by the skin of their teeth! A decision was made to halt construction of the Ishtugan Reservoir on the Belaya River, but then nothing of the

sort! A new subterfuge is invented. There is stubborn refusal to agree to lower the level of the Cheboksary Reservoir by 5 meters against the planned water mark, which might have saved a lot of land in long-suffering Povolzhye. And there are a host of such examples!

I do not at all concede that Chernobyl, the disaster in Armenia and other problems that have shaken our country in recent years are simply unfortunate coincidences. Their inception and shattering expansion were predetermined. The fact is that the number and scale of natural and industrial disasters are increasing throughout the world--this is the kind of uneasy time that we are living in. In our nation, considering the extremely poor quality of construction and of any goods, this hazard has to be squared. Therefore it is my view that nuclear electric power plants, tall dams like the one at Katunka and the Rogunskaya Dam and other structures that harbor the threat of a potential hazard are absolutely contraindicated for us at the moment.

So I am saying that we have in our nation an extraordinary ecological situation, the health of the people has been undermined and is still getting worse. Could it be that indeed in the place of the USSR there will be a "white substance of incomprehensible origin," such a shroud as appears in the fantasy of Eduard Limonov that is extremely realistic for me? Of course, as I did my best to explain to my American colleagues, the end of the world cannot occur in a single nation taken separately, especially if it occupies a sixth of the world's land area.

An extraordinary situation requires extraordinary approaches. And we hear: "The Congress of People's Deputies shall make a yearly assessment of the job done by the President of the USSR based on such criteria as the life expectancy and state of health of the nation's people, qualitative and quantitative parameters of national property left to posterity by society, and the contribution to preservation of the world and world civilization."

Such an eminently humanistic amendment to article 127 of the Law of the USSR on Instituting the Post of President is offered to the eyes of the entire nation by people's deputy of the USSR A. A. Zakharchenko, director of the Ukrainian school. The very essence is admirably captured.

And what happens? The Extraordinary Congress of People's Deputies turns down the amendment by a two-thirds vote. The overwhelming majority of the Congress turns a deaf ear to the health of the nation and the future of posterity. If I weren't the hardened woman that I am, I would simply burst into tears at this point.

But there has to be some of the human population that has a high instinct for self-preservation! No, I haven't the Government in mind. I don't believe it is going to "go green." Of course, it will "turn green," but only in a physical sense: no one is insured against bad air. But unfortunately, no true enlightenment is to be seen.

That is why I am convinced that a strong political force is needed. I'm talking about the "Green Party." They have already created a party in Lithuania, and have decisively declared themselves at the elections in the Ukraine. I have great hope that in the near future a "Green Party" will be formed in Russia as well, at least the people of Leningrad have already shown initiative.

What can be expected from this force? In my thinking, a radical social reorientation of our society. Absolute priorities were designated in A. A. Zakharchenko's proposal that was voted down by the Congress.

We must not delay in undertaking a series of special ecological programs, and foremost among them is a medical-biological program. Where are we going to get the money? From abolished departmental projects on a list that members of the "Green Party" are ready to offer.

As to assurance of a healthy economy, I would wholeheartedly sign a pre-election program of the "Democratic Russia" block. And among the primary measures I would name are

- -- unconditional elimination of industrial ministries;
- -- a moratorium on all giant construction sites and projects of the century;
- -- a thorough inventory of all production facilities and structures, and a decision on their fate from the standpoint of hazard to the population;
- -- conversion of not only military, but peacetime production facilities and ongoing construction projects, turning them to social needs;
- -- total overhaul of everything that we cannot do without;
- -- an exclusively competitive basis for all new projects and concepts under conditions of complete glasnost;
- -- curtailment of the importation into our country of ecologically dirty technologies and poisonous wastes of civilized nations.

Ecology must be given real priority over economy in the sense that no material goods can be bought at the cost of health and human lives.

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Detailed Study of Vibrational Relaxation of N_2O-Ar Mixtures Behind Shock Waves by Laser Schlieren Technique Using Infrared Diagnostics

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[Article by A. B. Zuyev and S. S. Negodyayev, Moscow Physicotechnical Institute]

[Text] The authors measure the time of vibrational relaxation behind an incident shock wave in mixtures of N_2O with Ar in the temperature range of 500-2370 K. The results are interpreted within the framework of a model with consideration of VV- and VT-processes of vibrational relaxation.

An analysis of data in the literature [1] gives an indication of the limited nature of currently available experimental material on rate constants of vibrational relaxation of N_2O. Among other things, until now there has been no investigation of VV-relaxation of the asymmetric mode of N_2O by Ar at temperatures of 800 K, where the method of laser fluorescence is no longer effective. Refinements are also needed for the rate constant of VT-relaxation of N_2O by Ar, as the results of recent measurements [2] obtained by using the laser schlieren method show a considerable difference of behavior of measured quantities $(P\tau)_c$ from the so-called "linear mixture rule" according to which

$$(P\tau)_c^{-1} = \psi_{N_2O}(P\tau^{N_2O})^{-1} + \psi_{Ar}(P\tau^{Ar})^{-1}, \quad (1)$$

where P is gas pressure, ψ_i is the molar fraction of the i-th component in the mixture, τ^{N_2O} is the time of vibrational relaxation of N_2O in a single-component mixture, and τ^{Ar} is the time of vibrational relaxation of N_2O with infinite dilution in Ar. The purpose of this research was to measure the time of vibrational relaxation of N_2O-Ar mixtures of various degrees of dilution at temperatures of 500-2300 K, using a laser schlieren method and infrared diagnostics. The laser schlieren method was used to study the evolution of density gradients caused by processes of energy exchange between vibrational and translational degrees of

freedom in a thermally excited gas, and infrared radiation was used to monitor the process of the change in population of vibrational levels of the ν_3 mode of N_2O

EXPERIMENT

Medically pure nitrous oxide and chemically pure Ar were used in the work. Mixtures were prepared with content of 30, 15, 7 and 3 percent N_2O and Ar. Upon admission to the facility, the mixtures were dried with phosphorus pentoxide. The gas was heated in a sectional stainless steel shock tube [3] with inside diameter of 50 mm and calibrated working channel 3 m long, and measurements were made behind the incident shock wave in a cross section 2.7 m away from the diaphragm unit. To minimize perturbations of gas flow in the plug, special steps were taken in coaxial installation of the shock tube sections, and the inspection ports in the measurement section were set flush with the walls of the working chamber.

Arrangements for measuring density gradients were set up in the following way: the beam of a single-mode LG-52-3 helium-neon laser with wavelength of λ = 0.637 nm directed at a right angle to the axis of the tube was focused by a collecting lens (f = 25 cm) on the center of the measurement cross section, where the gaussian diameter of the beam waist was 0.07 mm. Beam deflection caused by optical inhomogeneities in the relaxation zone and proportional to the longitudinal gradient of density of the gas along the axis of the tube was recorded from displacement of the laser spot to a distance of 0.6 m away from the tube outlet by a quadrant SI-2 photodiode. The signal from the load resistors of the photodiode was sent through followers to the differential input of an S8-17 memory oscilloscope. For load resistance of R_L = 3.6 kΩ, the coefficient of proportionality between beam displacement and oscilloscope signal was 962 mV/cm ± 20 percent. The time constant of the recording circuit measured by interruptions of the beam by an ML-3 Kerr shutter was 0.2 μs.

In addition to the schlieren arrangement, a channel for infrared diagnosis of radiation of the ν_3 mode (λ = 4.5 μm) was used in the same measurement cross section. This channel included a band filter (LiF), a lens set at twice the focal length from the axis of the tube (F = 30 cm), and a photoresistor (InSb) cooled by liquid nitrogen. The speed of the electronic circuit was better than 0.5 μs, and spatial resolution as determined by the size of the slit diaphragm at the tube outlet was ~1 mm.

To study relaxation both close to and far from equilibrium, the signals recorded by both diagnostic channels in each experiment were simultaneously fixed on the screens of two or three oscilloscopes with different specially set time sweeps and sensitivities. The initial pressure of the investigated gases was varied at a fixed shock wave velocity for the same purpose.

Two additional schlieren arrangements similar to that described above were set up at other points of the measurement section: one 2 mm upstream from the main one, and the other 200 mm downstream. The leading edges of the signals taken from these systems at the times of shock wave arrival were used as synchro pulses to trigger the measurement equipment and fix the time marks necessary for determining shock wave velocity. The initial pressure, pusher gas, material of the diaphragm and its thickness were varied in the experiment to get the necessary parameters of the gas in the plug that were calculated from the measured velocity and pressure preceding the shock. The initial temperature in the calculations was taken as 290 K.

RESULTS

In most experiments, the density changes recorded by each oscilloscope were near-exponential. Therefore, logarithmic processing of oscillograms yielded straight lines, and the slope of these lines was used to determine τ_{lab}: the time of change in signal amplitude by a factor of e in the laboratory coordinate system. For subsequent data analysis, the values of τ_{lab} were converted to quantities $(P\tau)_c$ characterizing vibrational relaxation in the coordinate system fixed to the shock wave front:

$$(P\tau)_c = P_2\tau_{lab}(\rho_2/\rho_1). \qquad (2)$$

Here P_2 is the equilibrium pressure behind the compression shock, (ρ_2/ρ_1) is the ratio of gas pressures preceding and following the shock, and τ is the relaxation time in the natural coordinate system. The use of two or three oscillograms simultaneously with the schlieren signal recorded in a different scale for determining τ_{lab} revealed several specific features of the relaxation process. It was found that the initial and final sections of the recorded profiles grad(ρ) after logarithmic processing were characterized by different quantities τ^1_{lab} and τ^2_{lab} ($\tau^2_{lab} > \tau^1_{lab}$) with a smooth transition between them. Comparative experiments were done in pure Ar with analogous modes of flow behind the shock wave to determine the contribution made to the observed signals by nonlinear deflections of the laser beam near the trough of the shock wave front. It was found that the effects of wave front

curvature are appreciable only at low pressures. Analysis of profiles grad(ρ) corresponding to greater difference from the beginning of relaxation in experiments at the same temperature but different pressures also confirmed that the result of measurements of the instantaneous value of $(P\tau)_c$ depends on the distance between the beginning of the processed section and the shock wave front. All "locally constant" times (Pτ) measured in this way are shown on Fig. 1-4 as functions of the Landau-Teller parameter $T^{-1/3}$, $K^{-1/3}$. Here T is the equilibrium temperature of the gas in the relaxation zone. Also given are times

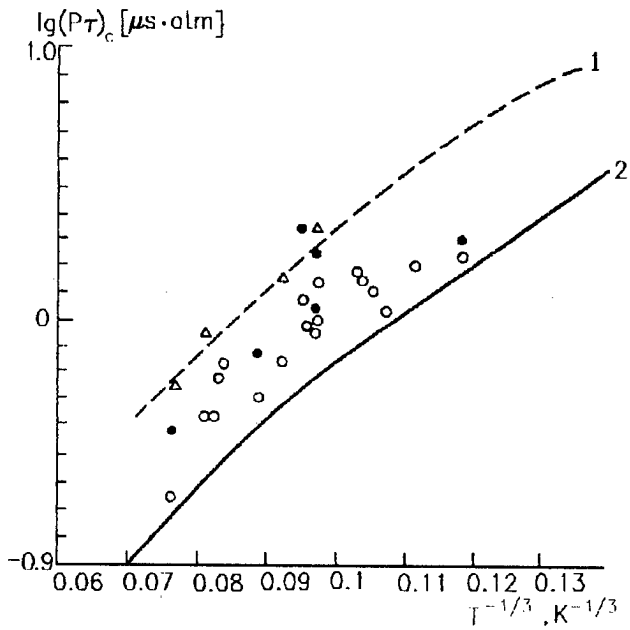

Fig. 1. Times of vibrational relaxation in a mixture of N_2O with Ar (3% N_2O + 97% Ar). Pressure P_2: 0.14-1.38 atm; o, •--times $(P\tau)_c$ obtained from processing of sections of the profile grad(ρ) on different relaxation stages; Δ--data for $(P\tau^{IR})_c$; 1--calculation of τ_2, 2--calculation of τ_1 with constants (25), (26) from our research and relaxation rates in a single-component mixture from [3]

$(P\tau^{IR})_c$ analogously determined from profiles of intensity of infrared radiation of the ν_3 mode in a mixture with 3 percent N_2O. The corresponding times τ^{IR}_{lab} that correspond to the given experiments and are used in subsequent analysis lie in a range of 0.95-2.0 μs and are at least twice the limit with respect to space-time resolution of the measurement circuit. Infrared diagnosis was not used for richer mixtures, as the available information was inadequate for explaining specific features observed in the experiment, such as the considerable

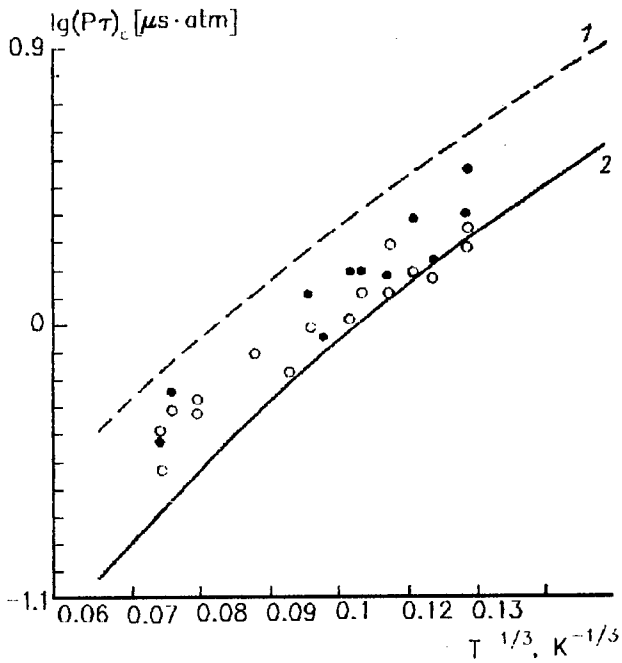

Fig. 2. The same as in Fig. 1 with a mixture of 7% N_2O with Ar. Pressure P_2 from 0.11 to 0.9 atm

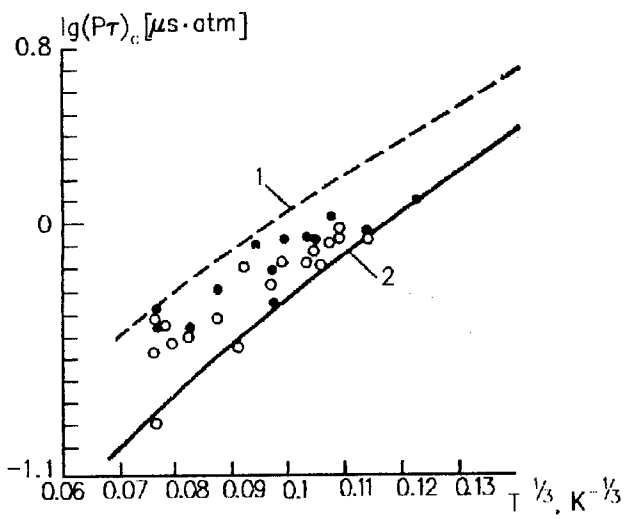

Fig. 3. The same as on Fig. 1 with a mixture of 15% N_2O with Ar. Pressure P_2 from 0.1 to 0.64 atm

ambiguity (by a factor of as much as 2-3) in relaxation times measured by the laser schlieren method, and the lack of coordination between the later and the results of infrared diagnosis. In particular, the relaxation times of the ν_3 mode $(P\tau^{IR})_c$ in some experiments were from double

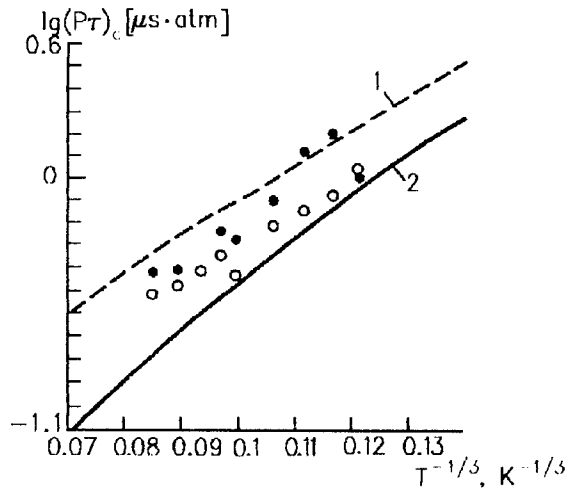

Fig. 4. The same as on Fig. 1 with a mixture of 30% N_2O with Ar. Pressure P_2 from 0.1 to 1.13 atm

to triple the VT-relaxation times, which could not be attributed to experimental error, estimated at 30 percent for $(P\tau^{IR})_c$, 10 percent for $(P\tau^1)_c$ and from 20 to 40 percent for $(P\tau^2)_c$ depending on N_2O concentration.

DISCUSSION

Vibrational relaxation times in N_2O-Ar mixtures were measured by a laser schlieren method in [2], where mixtures with 1, 4, 9 and 30 percent N_2O in Ar were studied. Comparison of the primary experimental material shows no contradiction between data on relaxation times $(P\tau)_c$ from the two papers for mixtures of similar composition. For example, times $(P\tau)_c$ from [2] for a mixture of 30 percent N_2O in Ar at a temperature of, let us say, T_2 = 750 K lie between the values of $(P\tau^1)_c$ and $(P\tau^2)_c$ measured in our research.

The peculiarities of N_2O vibrational relaxation observed in mixtures with Ar are not unexpected. Inconstancy of $(P\tau)_c$ during relaxation as determined from analysis of the profile grad(ρ) has been experimentally established for pure N_2O in [4] and earlier research [3]. However, there was no direct experimental conformation of the result in the cited studies by a method of measurements supplemental to the schlieren method.

The observed effect shows that ignoring the change of $(P\tau)_c$ in the relaxation process may introduce significant ambiguity into determination of such a generally accepted characteristic of binary collisions as

the time of relaxation of a polyatomic gas of type "A" in an infinitely dilute mixture with gas "B" by linear extrapolation of available experimental data using formula (1) to the limit $\psi_A = 0$. Generally speaking, the use of linear extrapolation will be correct for rate constants, but not for relaxation times. Therefore, determination of relaxation rate constants requires that we know the functional relation between the values of $(P\tau)_e$ measured in an experiment and the corresponding constants, and the specific form of the relation itself is determined by the degree of detail of the kinetic model.

In this connection, the data obtained in our research were explained within the framework of the following detailed model with allowance for relaxation processes:

$$N_2O(010) + M \overset{k_2^M}{\leftrightarrows} N_2O(000) + M, \tag{3}$$

$$N_2O(001) + M \overset{k_{321}^M}{\leftrightarrows} N_2O(110) + M, \tag{4}$$

which, as shown in [1], play a major role in vibrational energy exchange of pure N_2O for the investigated temperature conditions. Here (mnl) is the conventional notation for the numbers of excitation of levels in modes ν_1, ν_2 and ν_3 respectively of N_2O vibrations, M is the collision partner of the N_2O molecule, k_2^M and k_{321}^M are the rate constants of processes (3) and (4) for a collision with particle M. The mode approximation of [5] was used. According to this approximation, boltzmannian distribution exists in each i-th mode with respect to vibrational-rotational levels with instantaneous vibrational temperature T_{vi}, modes ν_1 and ν_2 being assumed in equilibrium ($T_{v1} = T_{v2}$) in view of the rapid VV-exchange between them in a quasiresonant process:

$$N_2O(100) + M \overset{k_{12}^M}{\leftrightarrows} N_2O(020) + M. \tag{5}$$

Since effects of anharmonicity of energy levels are insignificant for low degrees of excitation, N_2O molecules were modeled by a set of harmonic oscillators with characteristic temperatures of fundamental oscillations of 1848, 848 and 3202 K for modes ν_1, ν_2 and ν_3 respectively. In this case, vibrational relaxation can be described by the Biryukov-Gordiyets equations [6] that are nonlinear in the general case. However, if vibrations make a minor contribution to the total heat capacity of the gas, then there is almost no change of gas temperature during relaxation, and the equations can be considered linear. This is what happens in strongly dilute mixtures, and near the equilibrium state in the case of rich mixtures. Further interpretation of the experimental material was based on Biryukov-Gordiyets equations linearized in conjunction with equations of gas dynamics for processes (3), (4), which in this case took the form

$$-dx_i/dt = a_{i2}x_2 + a_{i3}x_3, \quad i = 2, 3, \tag{6}$$

where $x_i = (\varepsilon_i(T_2) - \varepsilon_i)/\varepsilon_i(T_2)$, ε_i and $\varepsilon_i(T_2)$ are the instantaneous and equilibrium number of vibrational quanta in the i-mode, the elements a_{ij} of the kinetic matrix being expressed in terms of rate constants of VT- and VV-relaxation in the form

$$a_{22} = \frac{1}{\phi}\left[\frac{9}{\theta_2^2}\frac{\epsilon_3(T_2)}{\epsilon_2(T_2)}k_{321} + \left(1 = \beta\psi_{N_2O}\frac{C_{v2}}{C_{tr}}\left(1 + 2\frac{\vartheta_2}{\vartheta_1}\frac{C_{v1}}{C_{v2}}\right)\right)k_2\right], \tag{7}$$

$$a_{23} = \frac{1}{\phi}\left[-3\frac{\theta_3}{\theta_2^3}k_{321} + \beta\psi_{H_2O}\frac{C_{c2}}{C_{tr}}\frac{\vartheta_3}{\vartheta_2}k_2\right]\frac{\epsilon_3(T_2)}{\epsilon_2(T_2)}, \tag{8}$$

$$a_{32} = -(3/\theta_2^2)k_{321}, \tag{9}$$

$$a_{33} = (\theta_3/\theta_2^3)k_{321}, \tag{10}$$

$$\varphi = 1 + (2\vartheta_2/\vartheta_1)^2 C_{v1}/C_{v2}, \tag{11}$$

$$\theta_i = 1 - \exp(-\vartheta_h/T_2). \tag{12}$$

Here ϑ_k, C_{vk} (k = 1-3) are the characteristic vibrational temperatures of modes of N_2O and their vibrational heat capacities, C_{tr} is the heat capacity of rotational and translational degrees of freedom, and the meaning of dimensionless parameter $\beta \simeq 1.0$ is discussed in more detail in [7].

The solution of the system of differential equations gives the profile of the density gradient in the relaxation zone as a sum of two exponential functions with relaxation times τ_1, τ_2 and weights S_1, S_2:

$$\mathrm{grad}(\rho(x, t)) = U_s^{-1}(\rho_2/\rho_1)\rho_2[S_1 \exp(-P_2t/\tau_1) + S_2 \exp(-P_2T/\tau_2)]P_2, \tag{13}$$

where t is time in the natural coordinate system ($t = (\rho_2/\rho_1)T_{lab}$), x is distance between the measurement cross section and the shock wave front, U_s is shock wave velocity, and τ_1 and τ_2 are determined from the relations

$$\tau_{1,2} = [a \pm (a^2 - 4b)^{1/2}]/2, \tag{14}$$

$$a = \alpha_1 k_{321} + \alpha_2 k_2, \tag{15}$$

$$b = \alpha_3 K_{321} k_2, \tag{16}$$

$$\alpha_1 = \frac{1}{\phi}\frac{\theta_3}{\theta_2^3}\left[\phi + \left(3\frac{\vartheta_2}{\vartheta_3}\right)^2\frac{C_{v3}}{C_{v2}}\right], \tag{17}$$

$$\alpha_2 = \frac{1}{\phi}\left[1 + \beta\psi_{N_2O}\frac{C_{v2}}{C_{tr}}\left(1 + 2\frac{\vartheta_2}{\vartheta_1}\frac{C_{v1}}{C_{v2}}\right)\right], \tag{18}$$

$$\alpha_3 = \frac{1}{\phi}\frac{\theta_3}{\theta_2^3}\left\{1 + \beta\psi_{N_2O}\frac{1}{C_{tr}}\left[\left(2\frac{\vartheta_2}{\vartheta_1}\right)C_{v1} + C_{v2} + \left(3\frac{\vartheta_2}{\vartheta_3}\right)C_{v1}\right]\right\}. \tag{19}$$

$$k_2 = \psi_{N_2O} k_2^{N_2O} + \psi_{Ar} k_2^{Ar} \quad (20)$$
$$k_{321} = \psi_{N_2O} k_{321}^{N_2O} + \psi_{Ar} k_{321}^{Ar}, \quad (21)$$

Here ψ_i is the molar fraction of the i-th component in the mixture, τ_1^{-1}, τ_2^{-1} are the eigenvalues of the matrix of kinetic coefficients a_{ij}, and S_1, S_2 are coefficients proportional to the contribution made to the total vibrational heat capacity by the mode responsible for relaxation time τ_i. Indeed, when $(k_{321}/k_2) < 1.0$, solution (14) permits the approximation

$$\tau_1^{-1} = \alpha_2 k_2, \quad (22)$$
$$\tau_2^{-1} = (\alpha_3/\alpha_2) k_{321}. \quad (23)$$

Hence we see that [one] of the relaxation times is due to VT-relaxation of a low-frequency oscillator (3), while the other is determined by the rate of intramode vibrational-vibrational exchange (4). Since a situation is realized in a mixture with 3 percent N_2O where relaxation of the ν_3 mode breaks away from VT-relaxation, and both times τ_1 and τ_2 are simultaneously recorded over a wide temperature range, relations (14)-(21) can be used for simultaneous determination of the rate constants of processes (3) and (4) for other mixtures where these conditions are not met, it is necessary to have a criterion that allows us to exclude from analysis "locally constant" times $(P\tau)_c$ obtained by processing oscillograms corresponding to the transition between τ_1 and τ_2. Such a criterion that is always explicitly or implicitly used in practice is satisfaction of linear expressions of the form (20), (21) in gas mixtures. In this connection, a procedure for determining the rate constants of processes (3), (4) in our research was constructed as follows. Taking the data for $(P\tau^{IR})_c$ as τ_2, and the lower limit of the set of experimental data $(P\tau)_c$ measured by the laser schlieren method in a three-percent mixtures as τ_1, the constants k_2^{Ar} and k_{321}^{Ar} were numerically selected for model (14)-(21) until the calculated and experimentally recorded relaxation times coincided. In doing so, the values of $k_2^{N_2O}$ and $K_{321}^{N_2O}$ known from [3] were used in formulas (20), (21), and the approximations for constants k_2^{Ar} and k_{321}^{Ar} are given as quadratic functions of parameter $T^{-1/3}$ of the type

$$k_i^{Ar} = 10^{\left(a_i T^{-2/3} + b_i T^{-1/3} + c_i\right)}, \quad (24)$$

where a_i, b_i, c_i are adjustment parameters determined from the entire set of experiments by the least squares method. Since measurements of $(P\tau^{IR})_c$ in our research were made at a temperature above 1000 K, a value of $(P\tau)^{-1} = (\theta_3/\theta_2^3) k_{321}^{Ar} = (8.0 \pm 1.1)\cdot 10^{-2}$ $(\mu s\cdot atm)^{-1}$ obtained by averaging the results of [8-11] in agreement with each other was taken to get an approximation of k_{321}^{Ar} of form (24) describing the available

experimental data over the entire investigated temperature range at T = 300 K. Similarly, the rate constant k_2^{Ar} at T = 300 K was also obtained by cumulative approximation in terms of point $k_2^{Ar} = 0.156 \pm 0.013$ $(\mu s \cdot atm)^{-1}$ corresponding to the most reliable data from [8, 12]. As a result, the approximations for the sought rate constants are expressed by the following relations:

$$(\theta_3/\theta_2^3)k_{321}^{Ar} = 10^{(236.47T^{-2/3} - 72.799T^{-1/3} + 4.503)} \ (\mu s \cdot atm)^{-1}, \quad 300 < T < 2360 \text{ K} \tag{25}$$

$$k_2^{Ar} = 10^{(-26.966T^{-2/3} - 14.255T^{-1/3} + 1.935)} \ (\mu s \cdot atm)^{-1}, \quad 300 < T < 2360 \text{ K} \tag{26}$$

and their graphs are shown on Fig. 5, where the measurements of other authors are also given for the sake of comparison. The factor (θ_3/θ_2^3)

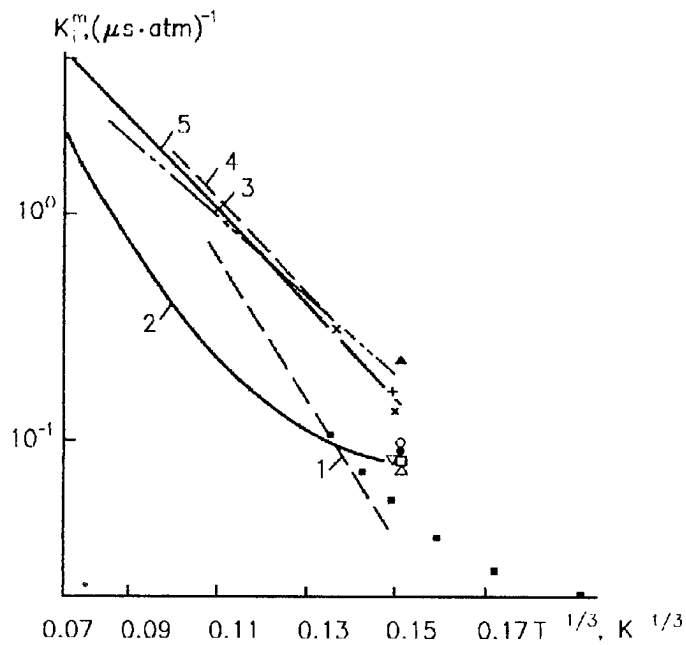

Fig. 5. N_2O relaxation rate constants for collision with Ar (k_2^{Ar}: 4--experiment [13], ▲--[14], +--[15], ∇--[16], ×--[12], 5--approximation (26), our research, 3--[2]; $(\theta_3/\theta_2^3)k_{321}^{Ar}$: o--experiment [8], ■--[17], •--[9], □--[10], Δ--[11]; 2--approximation (25), our research; 1--conversion of data from [18] by authors of [2]). Research techniques: acoustic (×, ▲), laser fluorescence (1, □, Δ, ■, ∇, •), pressure loss (+), shock tube (2, 3, 4, 5), spectrophone (0)

has been introduced in formula (25) for purposes of convenience in direct comparison of the results of our research with times of relaxation of the ν_3 mode of N_2O measured by the method of laser fluorescence and those related to constant k_{321}^{Ar} by the expression [1]

$$(P\tau_{321}^{Ar})^{-1} = (\theta_3/\theta_2^3)k_{321}^{Ar}. \tag{27}$$

A comparison of the resultant values for k_{321}^{Ar} shows that they agree on the whole with the body of data from other research. In particular, agreement with accuracy to a factor of 2 is observed when results found in [2] are extrapolated to the high-temperature region by recalculation of laser fluorescence measurements from [18], where N_2O-Ar-CO_2 mixtures were studied. Since the method of recalculation is not given in [2], and the final results with respect to k_{321}^{Ar} are not given in [18], we have interpreted the data from [2] as values of k_{321}^{Ar}, and shown them multiplied by (θ_3/θ_2^3) on Fig. 5. For a similar method of study in N_2O-Ar-CO mixtures, the authors of [17] give results for k_{321}^{Ar} that exceed the recalculated data from a previous paper [18] by a factor of 1.2-1.5 in the room temperature range. At the same time, the rate constant k_{321}^{Ar} obtained in [17] at room temperature does not agree with the data of a large body of experimental research [8-11] (see Fig. 5). It should be noted here that the authors of [17] likewise do not explain this discrepancy, including with their own earlier results [9]

Since leaner mixtures were studied in [17] (ψ_{N_2O} ~ 0.3 percent) than in [9] (ψ_{N_2O} ~ 3 percent), the discrepancy between the data obtained in the different mixtures can be interpreted as violation of the "linear mixture rule." However, we feel that the explanation is more likely associated with the need for considering a more detailed kinetic diagram of relaxation (e.g. accounting for the final rate of the process (5)) that complicates the functional relation between the measured times and the rate constants even without the assumption of violation of the "linear mixture rule," which agrees with preliminary conclusions of theoretical research [19, 20]. It is for this reason that the results of our research and the value of k_{321}^{Ar} averaged from [8-11] for temperature T = 300 K were used to get a smooth approximation that matches available experimental data throughout the investigated temperature range.

With respect to the rate constant of VT-relaxation, it can be said to agree well with a large body of data in the 400-500 K range. At the same time, there are certain discrepancies with some researchers at higher temperatures. In this context, it is of interest to make a comparison with the results of [2] obtained by the laser schlieren method, which are understated by a factor of 1.1-1.3 against our recommendations at T > 800 K. Analysis of similar experimental material

obtained in our research suggests that the given discrepancy can be attributed to an attempt by the authors of [2] to interpret data as VT-relaxation that were obtained from processing of sections of the profile grad(ρ) corresponding to transition to the phase of VV-relaxation. The latter statement is illustrated by Fig. 6, comparing a

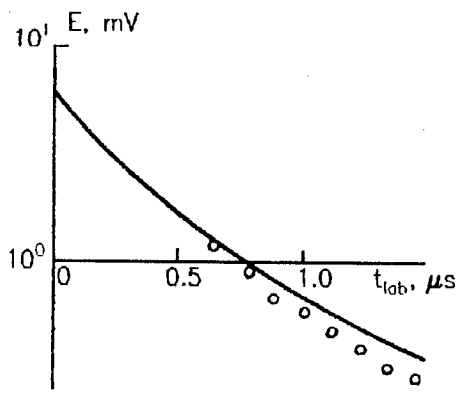

Fig. 6. Comparison of the calculated profile of density gradient with experiment. Mixture 3% N_2O + 97% Ar; E--amplitude of measured signal, points--experiment, solid line--calculation by formula A = ξKld grad(ρ) (x, t)), where ξ is the sensitivity of the recording circuit, K is the Gladstone-Dale constant for the mixture, l is the distance from the axis of the tube to the quadrant photodiode, d is the diameter of the tube; computational parameters: $S_1 = 3.144 \cdot 10^{-2}$ (μs·atm)$^{-1}$, $S_2 = 1.721 \cdot 10^{-2}$ (μs·atm)$^{-1}$, $(P\tau^1)_c = 0.322$ μs·atm, $(P\tau^2)_c = 0.932$ μs·atm, $T_2 = 1696$ K, $P_1 = 12.24$ Hg mm, $U_s = 1.287$ km/s, $(\rho_2/\rho_1) = 3.556$, $P_2 = 0.335$ atm

profile grad(ρ) recorded in the experiment with a profile calculated by formula (13) within the scope of the linear model with rate constants k_2^{Ar}, k_{321}^{Ar} taken from our research, and $K_2^{N_2O}$ and $k_{321}^{N_2O}$ taken from [3]. Since the ratio of the calculated relaxation times of this experiment is $(\tau_2/\tau_1) = 2.89$, and the ratio of their weights is $(S_2/S_1) = 0.56$, the section of transition from the fast to the slow phase is considerably stretched out in time, and logarithmic processing on the end segment gives a slight departure from the straight line, which was indeed recorded. The slight difference found between calculation and experiment can be eliminated by plane-parallel shifting of the graph along the time axis as a result of more precise referencing of the experiment to the beginning of relaxation.

Since the possibility of detecting the fast phase of relaxation is always limited by space-time resolution of the equipment, experiments at lower pressures are needed to study it. However, the role of boundary layers and curvature of the front becomes appreciable in this case, and therefore the relaxation times actually corresponding to the first phase could be measured only in a few experiments. It was the results of these experiments that enabled us to make correct use of rule (20) for determining the sought rate constants when matching the values of k_2 to the measured times, whereas the authors of [2] failed to record the fast phases, and as a result have cast doubt on the "linear mixture rule" itself. Proof that it remains valid, at least up to a degree of dilution of 3 percent, is given by the foregoing arguments, and also by the fact that calculation with the constants obtained in the given research satisfactorily explains both the dispersion of data measured by the laser schlieren method, and the time evolution of density gradients for all investigated mixtures (see Fig. 1-4, 6). A slight monotonic divergence between the high-temperature experiment and calculation by the linear model for mixtures with high N_2O content (see the example of Fig. 3) has been explained by the necessity of accounting for the change in temperature during relaxation, since the ratio of the complete heat capacity C_p to the heat capacity with frozen vibrational degrees of freedom C_p^* in a mixture of 15 percent N_2O at a temperature of, say, T_2 = 1930 K is $(C_p/C_p^*) = 1.20$, and the corresponding change in translational temperature of the gas during relaxation is ≈390 K, and at this point it is necessary to take consideration of nonlinear effects. For this purpose, the complete system of equations was numerically integrated for several experiments, followed by comparison of the solution for grad(ρ) with profiles obtained from the experiment. The results confirmed the applicability of the resultant rate constants for describing vibrational relaxation far from the equilibrium position as well.

Thus, in this research we have used the laser schlieren method and infrared diagnosis on a shock tube to measure vibrational relaxation times in mixtures of N_2O with Ar in the temperature range of 2500-2370 K. Two relaxation phases have been recorded in the evolution of density gradients behind the shock wave. One of these has been found to be due to VT-relaxation of the deformation mode of vibrations, while the other is due to the process of VV-exchange between modes ν_3 and $(\nu_1 + \nu_2)$. Interpretation of the experiments is based on a mode approximation within the scope of a linear model that accounts for the presence of VV- and VT-relaxation channels. Approximations have been obtained for rate constants that agree with those found in the literature. This is the first time that data have been obtained for VV-relaxation of N_2O in Ar at T > 800 K.

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Quasisteady Distributions in Shock Waves. Complete and Partial Distribution Functions of Molecules of SO_2 and NO_2

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[Article by L. V. Gayduchenya, I. S. Zaslonko and Yu. K. Mukoseyev, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, Moscow]

[Text] An experimental investigation is made of quasisteady distributions of vibrational energy of optically active states of electronically excited terms of SO_2 and NO_2 molecules in shock waves. A method is proposed and realized for reconstructing the total energy from partial distributions of optically active vibrations. Quasisteady solutions of the fundamental kinetic equation are analyzed within the scope of a step-by-step model of activation of a polyatomic molecule in thermal excitation.

A semiemperical method is described in [1] for reconstructing the distribution function (DF) of internal energy from the absorption-radiation spectra of polyatomic molecules based on analysis of the temperature and frequency dependences of spectral coefficients. The final result of measurements is the dimensionless DF

$$h_i(E_i, t) = f_i(E_i, t)/f_p(E_i),$$

where $f_i(E_i, t)$, $f_p(E_i)$ are the real and equilibrium (boltzmannian) distributions respectively.

Under conditions of thermal excitation in shock waves, the method allows us to follow the evolution of population of highly excited molecules (HEM) for times of t = 0.2-100 μs. Two stages can be distinguished in the decay of molecules: a rapid time-dependent stage (0.5-10 μs) due to processes of activation up to the barriers of chemical conversions of the HEM, and a slow phase due to the actual dissociation of molecules. During the second stage, the DF with respect to energy levels can be taken as quasisteady.

This paper discusses experimental data relating to the quasisteady stage of the distribution function for some polyatomic molecules.

Distributions obtained from analysis of "hot" absorption-radiation bands should be categorized as optically isolated effective vibration of the molecule in the ground (with respect to absorption) and electronically excited (with respect to radiation) states (so-called partial distribution functions (PDF) [1]).

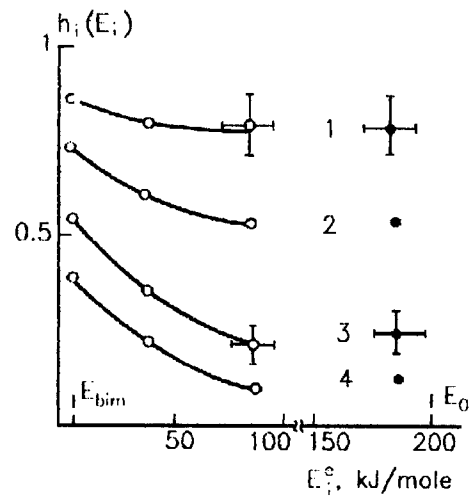

Fig. 1. Partial distributions with respect to vibrational energy of electronically excited term $^1B_1(SO_2)$ with thermal dissociation in shock waves at 3000 (1), 3500 (2), 4000 (3) and 4500 K (4). The solid dots are the population of term $^1B_2$; E_{bim}, E_0 are the positions of the barriers of bimolecular reaction and spontaneous decay respectively. Mixture--0.5% SO_2 in Ar

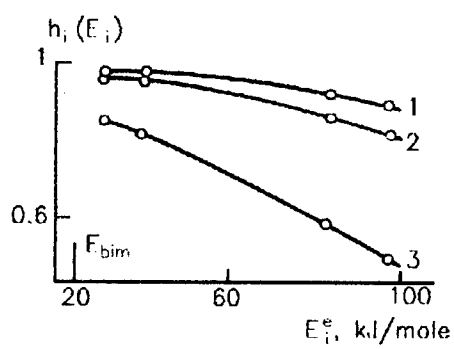

Fig. 2. Partial distributions with respect to vibrational energy of electronically excited term $^2B_1(NO_2)$ with thermal dissociation in shock waves at 2000 K. Content of NO_2 in mixture of NO_2 with Ar: 1--0.5, 2--1, 3--20%

Analysis of the experimentally determined PDF (Fig. 1, 2) enables us to trace the main features of behavior of $h_i(E_i)$ as a function of mixture composition and temperature. For example at $T < 3000$ K with strong dilution of SO_2 with inert gas, the relative population is close to equilibrium ($h_i(E_i) \approx 1$). With increasing T, there is a monotonic reduction in $h_i(E_i)$, indicating depletion of radiating states. The quantity $h_i(E_i)$ also decreases with an increase in partial content of SO_2 in the mixture. The vibrational energy E_i^e of the electronically excited state of $SO_2(^1B_1)$ is related [1] to the energy of level E_i determined in experiments by the expression

$$E_i = E_T + E_i^e,$$

where $E_T = 338$ kJ/mole is the energy of term $^1B_1$. The black dots on Fig. 1, in accordance with analysis of spectra of SO_2 [2, 3] denote the population of term $^1B_2$ that is separated from $^1B_1$ by an energy of ~170 kJ/mole.

We see from Fig. 1 that $h_i(E_i)$ is within the limits of the electronically excited term $^1B_1$, and also that the population of state $^1B_2$ at $T > 3000$ K is considerably less than the equilibrium distribution $h_i(E_i) = 1$. The only reason that equilibrium could be violated at $T > 3000$ K is that chemical reactions occur with participation of a highly excited molecule of SO_2.

The simplest kinetic scheme of the processes includes the following stages:

activation-deactivation

$$SO_2(^1A_1) + M \rightleftarrows SO_2^*(^1A_1) + M; \qquad (I)$$

internal conversion between the ground ($^1A_1$) and electronically excited term

$$SO_2(^1A_1) \rightleftarrows SO_2^e(^1B_1, {}^1B_2); \qquad (II)$$

by molecular reaction

$$SO_2^{e(*)} + SO_2 \rightarrow SO + SO_3; \qquad (III)$$

spontaneous decay

$$SO_2^{e(*)} \rightarrow SO + O \qquad (IV)$$

Stages (I) and (II) in the absence of chemical processes maintain boltzmannian distribution within the limits of the ground ($^1A_1$) and electronically excited terms. However, with an increase in temperature or in the partial content of SO_2, the rates of stages (III), (IV) become comparable with those of stages (I), (II), and the distribution function is distorted due to irreversible loss of excited particles.

Such is the qualitative pattern that explains the observed effects not only with dissociation of the SO_2 molecule, but NO_2 as well. We have processed primary experimental material on thermal excitation of NO_2 in shock waves [4, 5]. Fig. 2 shows the results of our analysis and data of [4, 5]. With respect to basic features, the behavior of $h_i(E_i)$ for the NO_2 molecule is similar to that for SO_2. It is notable that $h_i(E_i)$ is appreciably depleted even at energies considerably bellow the dissociation threshold ($E_o^{SO_2}$ = 546 kJ/mole, $E_o^{NO_2}$ = 305 kJ/mole).

This is not surprising for a high partial content of SO_2 and NO_2 in the mixtures, as the barriers of bimolecular reactions are considerably lower than those of dissociative reactions ($E_{bim}^{SO_2}$ = 335 kJ/mole, $E_{bim}^{NO_2}$ = 171 kJ/mole). In mixtures with a low content of the investigated molecules in the diluent gas (0.5 percent SO_2 and NO_2 in Ar), bimolecular reactions are insignificant, and depletion of $h_i(E_i)$ should be attributed to the occurrence of spontaneous decay on the corresponding energy levels. A question that arises in this connection is: how does depletion of the population at $E > E_o$ affect the energy levels of radiating states below the dissociation barrier?

The cause of this effect is to be found in the specifics of processes of energy exchange and chemical reactions of polyatomic molecules [6, 7]. The complete energy of a polyatomic highly excited molecule is rather rapidly redistributed among all vibrational degrees of freedom. The characteristic times of such intramolecular exchange for highly excited states are considerably shorter than the characteristic times of spontaneous decay, or the time between collisions of molecules [8]. Therefore, the rates of processes of activation and chemical transformations of HEM depend on the total energy, and consequently each degree of freedom of a polyatomic molecule makes its own statistical contribution to the process of activation or to overcoming the corresponding barriers of chemical reactions. in the classical case, the total energy is distributed evenly among S-degrees of freedom of the molecule.

As a rule, absorption emission diagnosis enables us to trace the population of individual types of vibration of the molecule, and appreciable depletion of the PDF at $E_i < E_o$ statistically reflects depletion of the DF with respect to total energy at $E > E_o$. In other words, the energy

level of an optically isolated vibration observed in the experiments as a result of rapid exchange of energy with other oscillators reflects the total store of energy of the HEM enabling reconstruction of the total store of energy of the HEM and the corresponding distribution function with respect to the total vibrational energy from the measured PDF of an individual vibration.

METHOD OF RECONSTRUCTING TOTAL DISTRIBUTION FUNCTION

The operation of reconstruction is based on the assumption that the time of observation of the PDF is sufficient for the total energy of the molecule to be redistributed randomly among all types of vibrations of the polyatomic molecule. The probability of detecting a molecule with energy E_i of a distinct type of vibration for a prescribed total energy is given by the conditional distribution function $\varphi(E_i/E)$ that is proportional to the number of states accessible for the prescribed E and E_i [6]:

$$\varphi(E_i/E) = \rho_i(\eta_i)\rho_{s-i}(E - E_i)/\rho_s(E).$$

Here $\rho_i(E_i)$ and $\rho_{s-i}(E - E_i)$ are respectively the density of states of the distinguished (i) and remaining (S - i) oscillators of the polyatomic molecule with number of normal modes equal to S, and $\rho_s(E)$ is the density of states of the molecule with total energy E. If the Whitten-Ravinovitch formula [9]

$$\rho_n(E) = \frac{\left(E + aE_{z_n}\right)^{n-1}}{(n - 1)\prod_n h\nu_i},$$

is used for the density of states, then we get for $\varphi(E_i/E)$

$$\varphi(E_i/E) = \frac{S - 1}{(E + aE_{z_s})}\left\{\frac{E = E_i + aE_{z_{(s-1)}}}{E + aE_{z_s}}\right\}^{S-2}, \qquad (1)$$

where a is a parameter close to unity and weakly dependent on E (see [9]);

$$E_{z_s} = 1/2 \sum_{h=1}^{s} h\nu_k$$

is the energy of zero-point vibrations.

Depending on the total energy, $\varphi(E_i/E)$ assumes a maximum value at $E = E_m$:

$$E_m = (S - 1)\left[E_i + aE_{z_i} - \frac{aE_s}{(S - 1)}\right],$$

$$\phi_{max}(E_i/E_m) = (E_i + aE_{z_i})^{-1}.$$

For a prescribed total energy, $\varphi(E_i/E)$ represents a so-called microcanonical distribution [6] with respect to the energy E_i of the distinguished type of vibrations. In accordance with this distribution, the energy E_i of the oscillator is not fixed, and may range from $E_i = 0$ to $E_i = E$ with probability that assumes a maximum value at $E_i = 0$.

The average value $\bar{E}_i$ is determined by averaging the possible values of E_i with respect to distribution (1):

$$\bar{E}_i = \int_0^E E_i\phi(E_i/E)dE_i. \tag{2}$$

After substituting (1) in (2) and integrating, we get an analytical relation between the average energy $\bar{E}_i$ of the distinguished type of vibrations and the total store of the energy of the molecule:

$$\bar{E}_i = \frac{E}{S}\left(\frac{E}{E + aE_z}\right)^{S-1}\left\{1 + \sum_{n=1}^{S-2}\frac{\prod_{k=0}^{n}(S - k)}{(n + 1)^n}\left(\frac{aE_{z_{S-1}}}{E}\right)^{S-(n+1)}\right\}. \tag{3}$$

Expression (3) implies that for sufficiently high levels of excitation of the molecule $E \gtrsim aE_z$, classical equal distribution of the total energy among the S-oscillators is valid:

$$\bar{E}_i(E \gtrsim aE_z) \simeq E/S.$$

We can easily go from conditional distribution (1) to canonical distribution by averaging $\Phi(E_i/E)$ with respect to the distribution of total energy f(E) [10]:

$$f_i(\bar{E}_i) = \int_{\bar{E}_i}^{\infty}\phi(E_i/E)f(E)\,dE, \tag{4}$$

where $f_i(\bar{E}_i)$, f(E) are respectively the partial and total functions of distribution of the ensemble of polyatomic molecules.

Expression (4) establishes a one-to-one relation between the PDF and DF and serves as a basis for reconstruction of the distribution function with respect to total energy.

For dimensionless function $h_i(E_i)$, we represent (4) as

$$h_i(\bar{E}_i) = \frac{Q_i(T)}{Q_s(T)} \int_{\bar{E}_i}^{\infty} h(E)\rho_{S-1}(E - \bar{E}_i) \exp\left(-\frac{E - \bar{E}_i}{RT}\right) dE, \qquad (5)$$

where $Q_i(T)$, $Q_s(T)$ are the partial and total vibrational statistical sums respectively. Within the framework of the assumed representation for $\rho(E)$, function $Q_k(T)$ is defined by the formula

$$Q_k(T) = \int_0^{\infty} \rho_k(E) \exp\left(-\frac{E}{RT}\right) dE = \frac{(RT)^k}{\prod_k R\Theta_k} \sum_{n=0}^{k-1} \frac{1}{n!}\left[\frac{E_{z_k}}{RT}\right]^n,$$

where Θ_k are the characteristic temperatures of the set of oscillators. It is implied by (5) that if the distribution with respect to total energy is equilibrium ($h(E) = 1$), then the PDF is equilibrium as well, i.e. $h_i(\bar{E}_i) = 1$. In the other limiting case of δ-distribution, $f(E) = \delta(E - E^*)$ (where E^* is the total excitation energy), the PDF is defined by microcanonical distribution

$$f_i(E_i) = \varphi(Ei/E^*).$$

To get the explicit dependence of $f(E)$ on $f_i(E_i)$, it is necessary to solve integral transformation (4). In the case of quantum oscillators, this cannot be done analytically. However, if we limit ourselves to comparatively high levels of total energy $E > E_{z_s}$, i.e. if we pass to the classical description of the density of states, then integral equation (5) is solved in analytical form relative to $h(E)$. We can readily see by direct substitution in (5) that the operator

$$h(E) = \frac{\left(\prod_{s-i} R\Theta_k\right) Q_s}{Q_i} \exp\left(\frac{E}{RT}\right) (-1)^{s-i} \frac{d^{(s-i)}}{dE^{(s-i)}} \left[h_i(E) \exp\left(\frac{-E}{RT}\right)\right]$$

is the solution of integral transformation (5).

As an example, for a polyatomic molecule with number of oscillators $S = 3$, we get

$$h(E) = h_i(E) - 2RTh_i'(E) + (RT)^2 h_i''(E),$$

where the total energy E is related to energy $\bar{E}_i$ of a selected oscillator by expression (3).

As we see, the total DF is determined not only by the absolute value of the PDF, but also by its (S - 1)-derivatives, i.e. it depends on the number of oscillators in the polyatomic molecule. In this connection, the procedure for reconstructing the DF from the PDF places certain requirements on the analytical approximation of the experimentally measured PDF. In particular, a satisfactory description of the PDF for SO_2 and NO_2 molecules was attained by a polynomial of second degree.

DISTRIBUTIONS OF TOTAL VIBRATIONAL ENERGY WITH THERMAL DECAY OF POLYATOMIC MOLECULES IN SHOCK WAVES

Let us turn to examination of specific representations of DF obtained with thermal heating of polyatomic molecules in shock waves. Fig. 3 shows the results of reconstruction of DF for SO_2 and NO_2 molecules as a function of the total vibrational energy E of electronically excited terms.

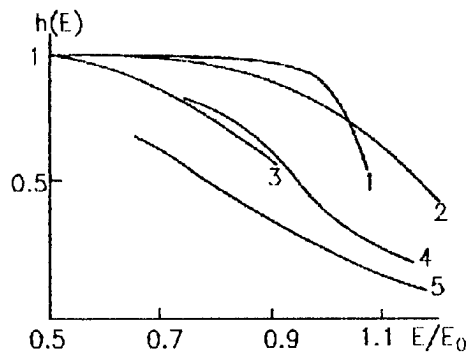

Fig. 3. Quasisteady distribution functions with respect to total vibrational energy for the ground state of molecules of CF_3I (1), N_2O (2), CO_2 (3) (results of processing of experimental data [11, 4] respectively) and for electronically excited terms of SO_2 (4) and NO_2 (5) (data of the authors and [4])

In the qualitative aspect, the behavior of distribution functions due to temperature and gas composition remain the same as for partial DF; significant deviations from equilibrium distribution are observed only near the corresponding barriers of chemical reactions. This result may serve in part as an argument in favor of the assumptions made above about the statistical nature of distribution of the total energy of HEM and about violation of equilibrium distribution in consequence of chemical reactions that take place with the participation of HEM. However, the simple formally kinetic model (I)-(IV) is incapable of quantitatively describing all details of the behavior of the DF, and in particular

depletion of the population on energy levels below the thresholds of chemical transformations. That this is a general phenomenon and is not due to PDF measurement error or problems with the technique of reconstructing the DF is illustrated by Fig. 3, showing results obtained by different methods (absorption, emission) for different polyatomic molecules.

Complete description of DF behavior of this kind necessitates more detailed investigation of the mechanism of activation of HEM, and in particular, departure from the assumption implicit in scheme (I)-(IV) about the so-called model of strong collisions, or a single-stage activation-deactivation process. The actual mechanism of activation of HEM is a step-by-step process and is characterized by the average energy $\langle\Delta E\rangle$ transferred in a single collision. In addition to this parameter that defines the energy transfer on the energy scale, and ultimately determines the form of the DF after each collision of an ensemble of relaxing molecules, consideration must be taken of the cross section or rate constant of relaxation (k_{rel}) of each level over the entire energy range. In conjunction with the rate constants of chemical reactions $k_0^{e(*)}(E)$, $k_{bim}^{e(*)}(E)$) and internal conversion (k_{E-V}), there are a minimum of seven parameters to be varied in the model.

We have done numerical and analytical modeling of the quasisteady stage of dissolution of the SO_2 molecule in shock waves based on solution of the principal kinetic equation within the scope of the "ladder" approximation for activation-deactivation processes. The details of the model can be found in [12]. We will mention here the general conclusions with respect to results of numerical modeling of DF (Fig. 4a, b).

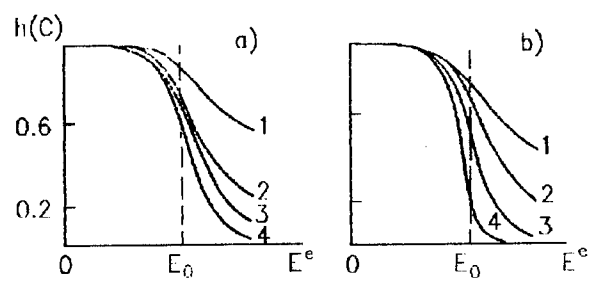

Fig. 4. Calculations of quasisteady distribution function with respect to total energy in thermal decay of SO_2. Parameters of the model: Φ_{sp}--ratio of rates of spontaneous decay to deactivation of the excited molecule on the reaction barrier E_0, $\langle\Delta E\rangle$--energy transferred in deactivating collisions: a--T = 3000 K; $\langle\Delta E\rangle$ = 20 kJ/mole, Φ_{sp}: 1--0.1; 2--0.3; 3--0.5; 4--1; 6--T = 3000 K, Φ_{sp} = 1; $\langle\Delta E\rangle$: 1--80, 2--40, 3--20, 4--8 kJ/mole

1. The degree of depletion of the quasisteady DF, as a rule, depends on combinations of variable parameters $\langle\Delta\varepsilon\rangle$, $k_o^{e(*)}(E)$, $k_{bim}^{e(*)}(E)$, $k_{E-v}(E)$, $k_{rel}(E)$, rather than on their absolute values. For example, the ratio of rates of the corresponding chemical reactions of HEM to the rate of their deactivation has the greatest effect on DF behavior in the region $E > E_o$, E_{bim}, while the ratio of parameters $\langle\Delta E\rangle/RT$ has the greatest effect for $E < E_o$, E_{bim}. When $\langle\Delta E\rangle \gg \max\{(E_o - E_{bim}), RT\}$ the DF in the prebarrier region is not distorted (limit of "strong" collisions).

2. The interpretation of DF for electronically excited states is further complicated by the fact that there are no quantitative data relative to the rate constants of internal conversion (k_{E-v}) for the investigated molecules of SO_2 and NO_2, and also by the unknown energy dependence of rate constants k_{rel}, $k_{bim}^{e(*)}$.

3. As a result of the large number of variable parameters and the aforementioned lack of information, an adequate description of the experimental DF can be achieved by different sets of combinations of these parameters (see Fig. 4), and therefore an experiment is needed in which these parameters would be measured in an independent way.

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Dynamic Effect when Hydrogen Atoms Recombine on the Surface of Semiconductors

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[Article by V. F. Kharlamov, V. N. Lisetskiy and G. G. Savelyev, Tomsk Polytechnic Institute]

[Text] The authors discover and study an effect of direct conversion of chemical energy of the recombination of atoms to mechanical energy in consequence of emission of fast H_2 molecules upon heterogeneous recombination of hydrogen atoms on the surface of germanium and zinc sulfide.

A considerable fraction of the energy released in heterogeneous chemical reactions may be carried off by a desorbed molecule in the form of electronic excitations, and the energy of vibrational, rotational, and translational motion [1-4]; in some cases a highly effective mechanism is electronic accommodation that results in electron-hole excitation of solids [5-8]; emission of electrons, ions and photons is also observed in the course of heterogeneous chemical reactions [8-12].

This paper describes an experimentally observed dynamic effect that arises upon heterogeneous recombination of hydrogen atoms on the surface of germanium and zinc sulfide in consequence of emission of H_2 molecules.

The desorption of molecules with epithermal kinetic energy may be due to a jump in the repulsive potential for molecules in the field of a solid surface; according to theoretical calculations, the fraction of energy of translational motion of molecules reaches 40 percent of the heat of reaction [13, 14]. Another mechanism of emission of fast molecules shows up in vibrational-translational transitions in the process of recombination of atoms (analogous to vibrational-translational relaxation in gases [15]). The formation of reaction products with excess translational energy has been observed in experimental research using

molecular beams [16-18]. In accordance with the law of conservation of momentum, desorption of molecules with epithermal kinetic energy is accompanied by a recoil force that acts on the solid. Previous attempts to measure this effect have been unsuccessful [19]. a recoil force has been successfully measured in the case of recombination of atoms on the surface of finely dispersed specimens on some metals, oxides and metal azides; a condition of reliable registration of the effect is the presence of a developed surface on the solid specimen.

The influence that the nature of the solid material and the method of producing it has on the magnitude of the recoil effect is discussed in [20]. The effect of a change in the state of the solid surface directly during measurement is of interest because of the problem of separating the recoil effect from accompanying gas-kinetic effects due to the presence of flows of thermalized atoms and molecules in the system. Another goal of our research was to study the mechanism of momentum transfer to the solid surface upon recombination of atoms. The subjects chosen for research were reactions of recombination of hydrogen atoms on the surface of zinc sulfide and germanium.

The surface of zinc sulfide may be in two states: the initial (juvenile) surface has adsorbed power with respect to molecules of H_2 [21, 22]; following treatment (conditioning) of the surface with atomic hydrogen, zinc sulfide does not adsorb H_2 molecules [23, 24]. When zinc sulfide interacts with atomic hydrogen, the state of its surface is changed by reduction [25], and possibly by amorphization [26]. Zinc sulfide also interacts with atoms of oxygen [27, 28]. Alternating treatment of ZnS with atoms of hydrogen and oxygen was used in our experiments to change the state of its surface.

Since molecules interact "repulsively" with the germanium surface, H_2 molecules are adsorbed on germanium in small amounts, adsorption is activated and apparently takes place with dissociation into atoms [29]. The temperature dependence of the coefficient of recombination of hydrogen atoms on face (111) of germanium implies that recombination of atoms leaves the "H_2 molecule-germanium" system in an excited state; some of the heat of reaction (about 16 percent) is expended on electronic excitation of the solid, or is carried off by desorbed H_2 molecules [30]. The surface of germanium is unstable in an atmosphere of atomic hydrogen: adsorption of hydrogen atoms reduces the electron population of the bonds between neighboring surface atoms of the crystal lattice, breaking them and forming a GeH_x compound [29, 31].

1. EXPERIMENTAL SETUP AND METHODS

Freshly pulverized finely dispersed phosphors ZnS-Mn (0.05%) and ZnS-Tm (0.1%) were used in the experiments. Powdered germanium was produced by milling undoped germanium single crystals with resistivity of 40 $\Omega \cdot$cm. The specific surface of the powders was 0.7-0.9 $m^2 \cdot g^{-1}$. The hydrogen was purified by diffusion through heated palladium and was continuously circulated at a pressure of 100 Pa through the vacuum chamber with the specimen. Atomic hydrogen was produced by electrodeless RF discharge in the gas; the hydrogen atoms passed from the discharge zone into the vacuum chamber through a glass tube. The concentration of atoms above the surface of the specimen as measured by a thermoprobe method [32] was 10^{13}-10^{15} cm^{-3}. In some experiments, oxygen was substituted for hydrogen. The vacuum chamber was placed in a thermostat, allowing the temperature of the specimen to be set in a range of 296-400 K.

The force F acting on the specimen was measured as atoms recombined on its surface. To do this, a thin film of 5 mg of powder was applied in the form of a spot 6-7 mm in diameter on the bottom of a glass dish 15 mm in diameter that was suspended on a quartz spring balance with sensitivity of $8 \cdot 10^{-8}$ N (the method of application of the specimen neutralized the radiometric effect, see below). In some experiments, a spring balance was used to measure the weight of hydrogen atoms adsorbed on the surface. For this purpose, the recoil force was compensated by applying the powder to both sides of a substrate held in the vertical plane.

In some experiments, the surface state of the zinc sulfide was monitored by determining the intensity of radical-recombination luminescence (RRL) excited upon recombination of hydrogen atoms on the surface of a phosphor (see [33]), and also the intensity of photoluminescence excited by a mercury-vapor lamp with wavelength of 313 nm. Luminescence intensity was recorded by an FEU-79 multiplier phototube.

2. EXPERIMENTAL RESULTS

Germanium. When the discharge in hydrogen is first switched on, a germanium specimen held in the horizontal plane is acted on by a force that is directed vertically downward; the magnitude of this force increases monotonically for ~10^3 s, approaching a steady-state value of $F \simeq 3 \cdot 10^{-6}$ N. The force vanishes or appears instantaneously when the discharge is subsequently turned off or on (Fig. 1). Conditioning of the specimen with hydrogen atoms at a temperature of $T \simeq 340$ K increases force F by a factor of roughly 1.5.

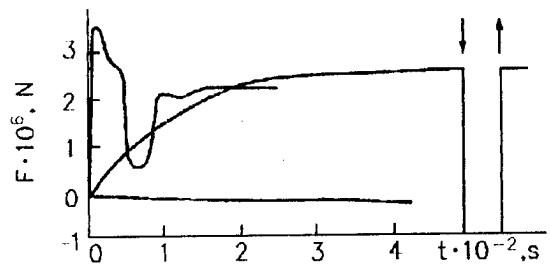

Fig. 1. Time dependence of the vertical component of the force acting on a substrate to which a thin film of finely dispersed germanium has been applied when it is held in the horizontal plane (1, 2) or vertical plane (3); 1, 3--freshly apply the specimen, T = 296 K; 2--after heating the specimen to a temperature of 360 K and cooling at a rate of $2 \cdot 10^{-2}$ $K \cdot s^{-1}$ to $T \simeq 330$ K. The arrows denote times of turning the source of hydrogen atoms off (↓) and on (↑)

The values of F are strongly dependent on temperature: when the specimen is heated, F drops to zero in a narrow temperature range of $340 \lesssim T \lesssim 360$ K. The curve of F(T) obtained during cooling of the specimen always lies considerably below the curve of F(T) obtained during heating (Fig. 2). On the cooling stage, curves F(t) recorded from the time of switching on the discharge are sharply non-monotonic (Fig. 1, curve 2). There is an increase in F with increasing concentration of atoms in the gas phase (Fig. 3, curve 1).

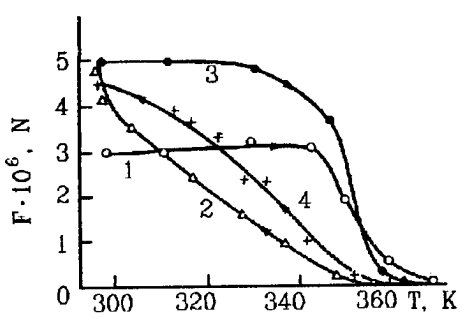

Fig. 2. Temperature dependence of force F acting in an atomic-molecular hydrogen atmosphere ($n = 6 \cdot 10^{20}$ m^{-3}) on a substrate to which a thin film of finely dispersed germanium has been applied: 1--first heating, 2--first cooling, 3--second heating, 4--second cooling. The rate of change in temperature is $2 \cdot 10^{-2}$ $K \cdot s^{-1}$

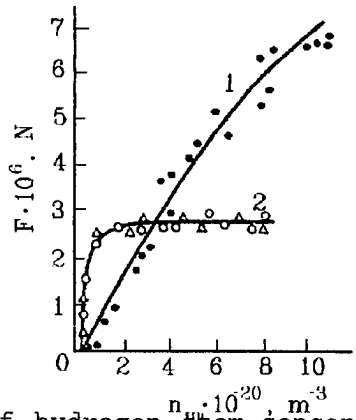

Fig. 3. Effect of hydrogen atom concentration on force F that acts in an atomic-molecular hydrogen atmosphere on a substrate with an applied thin film of finely dispersed germanium (1) or zinc sulfide (2). Points--experiment: •, o--at T = 296 K, Δ--at T = 373 K, solid curves--calculation by formulas (5)-(7)

The weight of the adsorbed hydrogen atoms is negligible ($\lesssim 10^{-7}$ N), and lies within the range of measurement error (Fig. 1, curve 3). The sensitivity of the balance also precluded registration of the adsorption of hydrogen molecules on germanium. Recombination of atoms on the surface of the specimens heated the substrate by 3-10 K. It was experimentally verified that the results of measurements of F were not influenced by evolution of heat (radiometric effect and Reynolds effect [34, 35]). No dynamic effect was produced by heating of the specimen with light from an incandescent lamp to a temperature of 400 K.

Zinc sulfide. Recombination of hydrogen atoms on the surface of freshly applied phosphor specimens is accompanied by bright luminescence; however, there is no recoil force in this case. The temperature curve of RRL intensity I passes through a sharp maximum; temperature dependence I(T) is reproduced for at least three cycles of heating of the specimen to 360 K with subsequent cooling to 296 K. Temperature cycling at $296 \lesssim T \lesssim (370\text{-}390)$ K gives rise to a recoil force of $3 \cdot 10^{-6}$ N (Fig. 4). The temperature curve for RRL intensity in this case changes sharply: the maximum on the curve disappears, and the behavior of I(T) coincides with the temperature dependence of intensity of photoluminescence (Fig. 5).

The new surface state of zinc sulfide for which heterogeneous recombination of hydrogen atoms produces a positive dynamic effect is stable, and is retained for at least $2 \cdot 10^5$ s. When the source of hydrogen atoms is

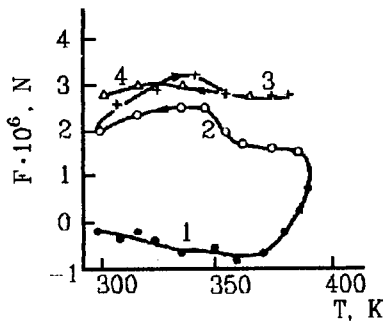

Fig. 4. Effect of temperature cycling on the force F that acts in an atomic-molecular hydrogen atmosphere ($n = 6 \cdot 10^{20}$ m^{-3}) on a substrate to which a thin film of finely dispersed zinc sulfide has been applied: 1--first heating, 2--first cooling, 3--second heating, 4--second cooling

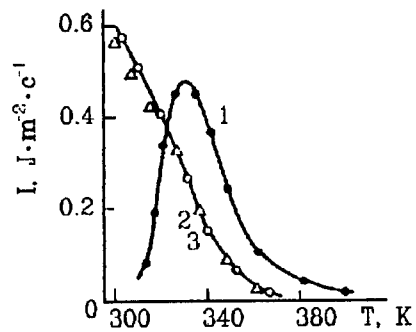

Fig. 5. Temperature dependence of RRL_H (1, 2) and intensity of photoluminescence (3) of phosphor crystal ZnS-Tm; $n = 1 \cdot 10^{20}$ m^{-3}, 1--prior to temperature cycling, 2--after cycling, 3--magnified 200 times

switched on and off, the recoil force changes instantaneously (curves of F(t) are Γ-shaped). With an increase in the concentration n of atoms in the gas phase, the recoil force first increases, and then is independent of n in the region of $n \gtrsim 1 \cdot 10^{20}$ m^{-3} (Fig. 3, curve 2).

When hydrogen is replaced by oxygen, there is no dynamic effect: $|F| < 1 \cdot 10^{-7}$ N. After treating a specimen with oxygen atoms, recombination of hydrogen atoms on the surface of zinc sulfide produces a small force F that increases slowly with time ($F > 0$). heating the specimen in an atomic hydrogen atmosphere at 390 K increases F.

3. DISCUSSION OF RESULTS

We can write the following expression for the force F acting on a substrate in consequence of recombination of atoms:

$$F = F_1 + F_2 + F_3 + F_4, \quad (1)$$

$$F_1 = \tfrac{1}{2}m\bar{v}J,\ F_2 = -\tfrac{1}{4}m\bar{u}J,\ F_3 = -\tfrac{1}{8}mS(\tfrac{1}{2}\bar{u}^2\Delta n - \bar{u}_M^2\Delta n_M), \quad (2)$$

$$\Delta n \simeq 2\Delta n_m \simeq \tfrac{1}{4}\gamma n\alpha, \quad (3)$$

$$J = \tfrac{1}{4}n\bar{u}\gamma\alpha S. \quad (4)$$

(The direction of the recoil force is taken as positive.) Here F_1 is the recoil force caused by desorption of molecules formed upon recombination of atoms; F_2 is the force that arises in consequence of the difference between the flows of adsorbed atoms to the two opposite sides of the substrate; F_3 is the force caused by unequal pressure of gas on the top and bottom surfaces of the substrate in consequence of the difference in concentrations of atoms (Δn) and molecules (Δn_M) on the two sides of the substrate; F_4 is caused by heating of the specimen upon recombination of atoms [20, 34, 35]; J is the reaction rate of recombination of atoms; $\bar{u}$, $\bar{u}_M$ are the velocities of thermal motion of atoms and molecules in the gas phase; $\bar{v}$ is the average value of the projection of the velocity of desorbed molecules on the normal to the surface; n, n_M are the concentrations of atoms and molecules in the gas phase; m is the mass of a molecule; S is surface area of the specimen; α is a coefficient that accounts for the actual surface on which recombination takes place; γ is the coefficient of recombination of atoms on the surface of the specimen.

According to theoretical estimates and experimental results, the value of F_4 is negligible. The rate of sputtering of germanium and zinc sulfide by hydrogen atoms is minor ($\sim 10^{-5}$ mg·s^{-1}); sputtering cannot have any noticeable effect on measurement results. Consequently, the dynamic effect is determined by F_1-F_3. By using expressions (1)-(4) and Maxwell distributions for hydrogen atoms and molecules, we get ($\bar{u}^2 = 2\bar{u}_M^2$)

$$F \simeq F_1 + F_2 + F_3 \simeq F_1 + 1.125F_2 = \tfrac{1}{2}mJ(\bar{v} - 0.8\bar{u}_M). \quad (5)$$

Research results show that the magnitude of the dynamic effect depends on the material of the specimen, the state of its surface, the recombination rate, and the type of recombining atoms.

Germanium. The final relations (Fig. 1-3) can be interpreted as follows. In an atmosphere of hydrogen atoms, molecules adsorbed from the air are cleaned from the germanium surface, reactions of adsorption and

recombination of hydrogen atoms take place, and the force F arises as the sum of recoil momenta transferred to the surface upon desorption of fast H_2 molecules. The form of temperature curves F(T) (Fig. 2) and the nomonotonic behavior of kinetic changes F(t) (Fig. 1, curve 2) are probably associated with the unstable state of the germanium surface with adsorbed layer of hydrogen atoms (see [29, 31]). With a change in temperature, apparently due to a structural phase transformation, the surface changes from state (Ge•xH) to state (GEH_x), resulting in an abrupt change in the probability of emission of fast molecules.

According to experimental results, hydrogen atoms recombine on face (111) of germanium by the Langmuir-Hinschelwood mechanism [30]:

$$H + Z \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} HZ, \quad HZ + HZ \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} H_2 + 2Z, \tag{I}$$

where Z is the adsorption center, k_1-k_2' are the rate constants of the reactions. Using mechanism (I), we can write the following expression for the reaction rate:

$$J = k_2 N^2 \alpha S,$$
$$N = \frac{k_1 + k_1' + 4k_2' N_0}{2(k_2 - k_2')}\left[\left(1 + \frac{4N_0(k_2 - k_2')(k_1 + 2k_2' + 2k_2' N_0)}{(k_1 + k_1' + 4k_2' N_0)^2}\right)^{1/2} - 1\right]; \tag{6}$$

here N is the concentration of adsorbed atoms, N_o is the concentration of adsorption centers, $k_1 = \frac{1}{4}n\bar{u}\sigma$, σ is the adsorption cross section of a hydrogen atom.

On the initial linear section of F(n) (see Fig. 3, curve 1) when conditions [30]

$$k_1 \gg k_1' + 4k_2' N_o, \quad k_2 \gg k_2' \tag{7}$$

and inequality $4k_2 N_o \gg k_1$ are met, according to (4), (6) we have $N \simeq (k_1 N_o)^{1/2} k_2^{-1/2}$, $\gamma = \gamma^* \simeq \sigma N_o$; using values of $N_o = 7.4 \cdot 10^{18}$ m^{-2} [36], we get $\gamma^* = 8.8 \cdot 10^{-2}$. Assuming $n = n^* = 1 \cdot 10^{18}$ m^{-3}, $\gamma = \gamma^* = 8.8 \cdot 10^{-2}$, $F = F^* = 1 \cdot 10^{-6}$ N, $\bar{u} = 2.5 \cdot 10^3 m \cdot s^{-1}$ and using expressions (4)-(6), we find

$$F(n) = \frac{JF^*}{J^*} = \frac{4k_2 N^2 F^*}{\bar{u} n^* \gamma^*} = 1.8 \cdot 10^{-28} k_2 N^2. \tag{8}$$

When conditions (7) are met, relation (8), where the expression for N takes the form (6), coincides with the experimental relation (Fig. 3, curve 1) if $k_2 = 6 \cdot 10^{-11}$ $m^2 \cdot s^{-1}$.

Assume that condition $\alpha \gtrsim 70$ is satisfied as in the case of zinc sulfide (see below). Using expressions (4), (5) and the value $S = 3\cdot10^{-5}$ m^2, we find $1.4\cdot10^3 < \bar{v} \lesssim 1.5\cdot10^3$ m$\cdot$s^{-1}; in this case, a fraction of the heat of reaction equal to $f = mv^2/2D = 2m\bar{v}^2/D = 2\cdot10^{-2}$ is converted to kinetic energy of motion of H_2 molecules, where v is the average velocity of desorbed H_2 molecules, D is the liberation of energy upon recombination of two hydrogen atoms. (The angular distribution of momenta of the desorbed molecules is taken as uniform.)

Zinc sulfide. The change in surface state of zinc sulfide under the action of H_2 molecules where the quantity $\bar{v} - 0.8\ \bar{u}_M$ changes sign (see (5)) and there is an abrupt increase in recoil force (Fig. 4, curve 1), as well as adsorption measurements (23, 24) show a correlation between the adsorption power of the surface of ZnS with respect to H_2 molecules and the nonlinear recoil force. At room temperature and above, no bound dissociativeless states of hydrogen molecules are detected on the surface of zinc sulfide conditioned by hydrogen atoms; molecules interact "repulsively" with the surface. This can be attributed to accumulation of donor centers on the ZnS surface upon reduction by hydrogen atoms [25] (e.g. in the reaction $2H + Zn^{2+}S^{2-} \rightarrow H_2S + Zn^+V_s^-$, where V_s^- is a sulfur vacancy). In consequence of the three-electron nature of the bond with these centers (Zn^+, V_s^-), H_2 molecules on the surface of ZnS are in an energetically advantageous repulsive state.

The presence of a plateau on the curve F(n) (Fig. 3, curve 2) is a consequence of the limitation in reaction rate when atoms recombine by the Langmuir-Hinschelwood mechanism [21, 24, 37]. Using expressions (5)-(7) (conditions (7) are satisfied according to data of [24]), we find that the theoretical curve F(n) describes experimental results (Fig. 3, curve 2) with satisfaction of equality $\sigma(k_2N_o)^{-1} = 3.2\cdot10^{-22}$ m$^2\cdot$s.

It is known that $\bar{v} \geqq 0.5\ \bar{u}_M$. Therefore, on the basis of expression (5), we can write the inequality $|F| \leqq 0.15m\bar{u}_M J$; for negative values of force F. Hence, using (4), we find

$$\alpha \geqq 4|F|(0.15m\bar{u}_M n\bar{u}\gamma S)^{-1}.$$

Assuming as an estimate $\sigma = 10^{-20}$ m^2; $N_o = 10^{19}$ m^{-2}, $k_2 = 3.1\cdot10^{-18}$ m$^2\cdot$s, $F = -6\cdot10^{-7}$ N (Fig. 4), $n = 6\cdot10^{20}$ m^{-3}, from equality

$$J = k_2N_o^2\alpha S = \tfrac{1}{4}n\bar{u}\gamma\alpha S$$

we get $\gamma \simeq 8.4 \cdot 10^{-4}$, which corresponds to experiment [38, 39]; this gives $\alpha \gtrsim 70$. Using expressions (4), (5) and a value of $F = 3 \cdot 10^{-6}$ N (Fig. 4), we get $1.4 \cdot 10^{3} < \bar{v} \lesssim 3.9 \cdot 10^{3}$ $m \cdot s^{-1}$, $0.02 <! \lesssim f \lesssim 0.15$.

The result $\alpha \gg 1$ means that the atoms recombine on the surface of fine particles of zinc sulfide located not only on the surface, but also within the powder film. In this process, fast H_2 molecules undergo elastic collisions during diffusion toward the surface of the film (loss of kinetic energy in collisions with a solid is small because of the considerable difference between the mass of the H_2 molecule and that of the surface atoms of the solid). Due to repeated collisions with fine particles of powder, the angular distribution of the momenta of fast particles leaving the film can be considered uniform. The condition $\alpha \gg 1$ apparently explains why the dynamic effect has not been observed in compact materials [19].

CONCLUSION

Recombination of hydrogen atoms of finely dispersed germanium and zinc sulfide is accompanied by a dynamic effect (recoil effect) caused by desorption of fast H_2 molecules. The recombination reaction that gives rise to the dynamic effect takes place not only on the surface, but also beneath the surface of the powder film, magnifying the recoil force by a factor of tens, the magnitude of this force being determined by the sum of momenta of H_2 molecules. In consequence of the inhomogeneity of the powder surface, these molecules have uniformly distributed momenta. The dynamic effect is detected because of the high catalytic activity of finely dispersed specimens that have a developed surface. It cannot be ruled out that molecules with epithermal velocities are formed mainly on identical faces of fine single crystals of powder. A change in the surface state of zinc sulfide when it is treated with atoms of hydrogen or oxygen sharply changes the magnitude of the dynamic effect.

In accordance with the conclusions of [21, 30, 37], the results can be used to describe the reaction of recombination of hydrogen atoms on the surface of germanium and zinc sulfide by Langmuir-Hinschelwood mechanism (I). In this context, the maximum fraction f of chemical energy of recombination converted to mechanical energy (elastically deformed balance spring) was: $f \simeq 2 \cdot 10^{2}$ for germanium, $0.02 \lesssim f \lesssim 0.15$ for zinc sulfide.

Registration of the dynamic effect might be used as a method of monitoring the surface state of solids.

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